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GEOCHIMICA ET COSMOCHIMICA ACTA

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Trace elements in a suite of Hawaiian lavas

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ABSTRACT

Analyses for trace elements of a series of Hawaiian lavas from olivine basalt to trachyte are given and comparisons made with data from the Skaergaard intrusion, East Greenland. The results are in conformity with the view that the Hawaiian series are essentially the result of fractional crystallization.

Recent work by MACDONALD and STEARNS (1946, 1949a, 1949b) has carried our knowledge of the petrography and petrogenesis of the igneous rocks of the Hawaiian Province a clear step forward. Using new mineralogical data and the many high quality chemical analyses available, the series from olivine basalt through andesine "andesites" to oligoclase "andesites" and trachytes, is established as dominantly the result of fractional crystallization. The purpose of this paper is to record the variation in certain trace constituents in this series and to compare it with that resulting from fractional crystallization of basic magma in the Skaergaard intrusion of East Greenland (WAGER and MITCHELL, 1951).

DALY (1944) and TILLEY (1950, pp. 39–46) have considered the relation of the Hawaiian rock series to the rocks of the Thulean and other provinces. This is a problem to which trace element investigation should be able to contribute. In the present paper, however, all that is attempted is to indicate the changes in trace element content in the limited series of rocks for which an origin by crystal fractionation is broadly established.

The spectrographical determination of the trace element has been carried out by one of us (R. L. M.) at the Macaulay Institute for Soil Research, Aberdeen, using the same techniques as for the Skaergaard rocks with which the main comparisons are made (WAGER and MITCHELL, 1951). We are indebted to the Director of the Macaulay Institute for permission to carry out this work.

To Dr. G. A. MACDONALD we are grateful for the gift of specimens and for his agreement with the project of their further analysis.

TRACE ELEMENTS IN THE HAWAIIAN ROCKS

The results for the trace elements are presented in Table I along with analyses for the major constituents quoted from MACDONALD (1949b). In addition three new analyses for trace elements of mugearite and trachyte from Skye are given. The trace element determinations in the Hawaiian and Skye rocks were made at the same time and the method employed was similar to that used for the Skaergaard rocks, so that the results should be directly comparable. The recent report by AHRENS (1951) suggests that these results should be reasonably comparable, within the

Table 1. *Trace elements in lavas from Hawaii and the Isle of Skye* (Trace element determinations by R. L. Mitchell)

		Hawaii									*Skye*		
	S	*A* Picrite basalt	*B* Picrite basalt	*C* Olivine basalt	*D* Basalt	*E* Basalt	*F* Andesine andesite	*G* Andesine andesite	*H* Oligo-clase andesite	*I* Oligo-clase andesite	*J* Soda trachyte	*K* Mugearite H·4098	*L* Mugearite H·4096	*M* Trachyte H·359
		Major constituents as weight per cent of the oxide												
SiO_2		47·25	49·27	50·52	52·28	51·55		50·68	51·99	52·27	62·02			
Al_2O_3		9·07	9·38	13·85	10·83	13·59		16·42	16·30	17·05	18·71			
TiO_2		1·61	2·58	3·63	4·43	1·98		2·64	3·02	2·13	0·31			
Fe_2O_3		1·45	1·28	0·98	1·90	2·33		5·79	2·75	3·51	4·30			
MgO		19·96	17·74	7·07	7·69	8·02		4·25	3·19	3·13	0·40			
FeO		10·41	10·31	9·77	9·30	9·04		6·22	7·44	7·20	0·10			
Na_2O		1·38	1·80	1·51	2·29	2·43		4·70	5·64	5·40	6·90			
CaO		7·88	7·46	11·33	10·03	10·31		6·47	6·67	5·82	0·86			
K_2O		0·35	0·42	0·47	0·51	0·27		2·16	2·13	2·22	4·93			
P_2O_5		0·21	0·26	0·22	0·32	0·24		0·17	1·25	0·62	0·24			
MnO		0·13	0·09	0·14	0·12	0·12		0·22	0·11	0·16	0·15			
		Trace constituents as parts per million of the element												
Be		—	—	—	—	—	—	—	—	—	8	—	5	—
Ga	1	15	20	25	25	20	20	20	25	20	25	25	20	25
Cr	1	1000	2500	400	500	500	—	—	—	—	20	—	—	—
V	5	300	200	400	250	200	70	70	30	8	—	50	7	15
Mo	1	1	2	—	1	—	—	—	—	—	4	—	—	—
Li	1	1	1	1	1	3	20	10	15	25	30	15	20	30
Ni	2	400	1500	80	100	70	6	7	10	15	15	3	15	15
Co	2	70	80	30	40	30	12	16	7	4	2	20	3	2
Cu	10	150	150	200	100	200	<10	<10	<10	<10	<10	<10	<10	<10
Sc	10	—	—	10	10	10	—	—	—	—	—	—	—	10
Zr	10	100	50	100	50	150	300	400	1000	1500	1500	200	2000	1500
Y	20	20	20	20	25	20	60	50	150	100	150	80	200	200
La	20	—	—	—	—	—	30	20	70	150	100	30	150	250
Sr	10	400	200	800	600	1000	2000	3000	4000	3000	100	1000	800	250
Ba	5	150	70	150	100	100	600	600	1000	1000	800	1500	2000	3000
Rb	20	—	—	—	—	—	40	30	70	40	300	20	100	150

A. Picrite basalt Kilauea, lava flow of 1840, Nanawale Bay. Analyst for major constituents, G. Steiger. (Also reported NiO—0·09, BaO—None, SrO—None, ZrO_2—None.) (Macdonald, 1949, p. 74, No. 1.)
B. Picrite basalt Mauna Loa, lava flow of 1868. Analyst for major constituents, H. S. Washington. (Also reported CO_2—None.) (Macdonald, 1949, p. 63, No. 8.)
C. Olivine basalt Kilauea, 1919 lava flow at north-east edge of caldera floor. Analyst for major constituents, J. J. Fahey. (Also reported NiO—Trace.) (Macdonald, 1949, p. 74, No. 12.)
D. Basalt Mauna Loa, lava flow of 1859. Analyst for major constituents, H. S. Washington. (Macdonald, 1949, p. 63, No. 12.)
E. Basalt Mauna Loa, lava flow of 1926, at 1,400 feet altitude near highway. Analyst for major constituents, E. S. Shepherd.(Macdonald, 1949, p. 63, No. 9.)
F. Andesine andesite Mauna Kea, west slope Mauna Kea.
G. Andesite Mauna Kea, Laupahoehoe volcanic series: Laupahoehoe peninsula, at sea level. Analyst for major constituents, H. S. Washington. (Macdonald, 1949, p. 83, No. 10.)
H. Oligoclase andesite Kohala, Hawi volcanic series, 2,900 ft at Moumoualoa Gulch. Analyst for major constituents, H. S. Washington. (Macdonald, 1949, p. 87, No. 11.)
I. Oligoclase andesite Kohala, Hawi volcanic series, 3,600 ft altitude at Puu Makea. Analyst for major constituents, H. S. Washington. (Macdonald, 1949, p. 87, No. 12.)
J. Trachyte Hualalai, Puu Anahulu. Analyst for major constituents, H. S. Washington. (Also reported BaO—0·02, CO_2—None, Cl—None, SO_3—0·02.) (Macdonald, 1949, p. 78, No. 8.)
K. Mugearite H·4098, lower unit of uppermost composite lava, Roineval, Isle of Skye.
L. Mugearite H·4096, roadside, C.130 ft O.D., west side of Knock Garsin, Bracadale. Isle of Skye.
M. Trachyte H·359, roadside, C.400 ft below Ros a' Mheallain, 2 miles N.E. of Bracadale, Isle of Skye.

$\pm 50\%$ accuracy of the semi-quantitative technique, with spectrographic trace element determinations from other sources. The Hawaiian rocks are classified under the names given by MACDONALD and the different groups are sufficiently similar in trace element constituents for averages to be taken (see Table II).

The picrite basalts are characterized by high Cr and Ni, compared with the rocks classified as basalt or olivine basalt. Ni is no doubt largely present in the abundant olivine and pyroxene. High Cr usually goes with the olivine-rich rocks, but it is not certain in which minerals the Cr is contained. It may be present in a separate chrome spinel phase as found in the gabbro picrite of the Skaergaard intrusion. The presence of Cr in the olivine structure is doubtful but it is certainly a relatively abundant constituent of early pyroxene. The picrite basalts are interpreted as resulting from the enrichment of basalt by early addition of olivine crystals, as in the Skaergaard gabbro picrite with which they may be compared (Table II).

The sequence from basalt to trachyte may be taken as an approximation to the line of liquid descent and the change in trace elements may be considered from this point of view. Over the range basalt—andesine andesite—oligoclase andesite* the dominant minerals are olivine, clinopyroxene, plagioclase and iron ore and, except for olivine, these are present in all members of the series. The changes in trace elements reflect, in a complex way, changes in the composition of these solid solution series during fractionation. Some of the main changes in the series from basalt to oligoclase andesite will be first noted and then the further change in passing on to the trachyte stage will be discussed.

Over the limited range from basalt to oligoclase andesite there are certain elements which show significant decreases which, in parts per million, are: Cr from 500 to < 2; V from 300 to 20; Ni from 80 to 6 followed by a rise to 12; Co from 30 to 5; Cu from 200 to < 10. Apart from Cu these are elements which tend to be strongly or moderately strongly concentrated in early ferromagnesian minerals. Another group of elements increase in amount, moderately strongly or strongly, over the same range: Li from 2 to 20; Zr from 100 to 1200; Y from 20 to 120; La from < 20 to 100; Sr from 800 to 3500; Ba from 120 to 1000; Rb from < 20 to 50. Except for Sr, these are elements the bulk of which presumably remains in successive residual liquids, since they enter only to a limited extent into the plagioclase, pyroxene, olivine and iron ores which are the chief crystal phases forming over this range. Sr is rather different as it is known to enter readily into plagioclases of intermediate composition, such as occur in the andesite and oligoclase andesite. Ga and possibly Mo are the only two elements estimated which change only slightly in amount.

For many of the trace elements there are several fold changes in abundance in passing from basalt to oligoclase andesite; the changes in the major constituents are usually much smaller. Thus while the percentage changes in certain of the major constituents are: SiO_2 from 50 to 52, MgO from about 8 to 3, FeO from about 10 to 6, Na_2O from about 1·5 to 5·5, there is a change of 200 times for Cr, 15 times for V, 10 times for Li, 10 times for Ni, etc. The magnitude of the changes for

* The term andesite is not entirely appropriate for these rocks (Cf. TILLEY, 1951, p. 41) but will be used here following the usual Hawaiian practice.

Table 2. Average values for trace elements in lavas from Hawaii and in certain rocks and residual magmas of the Skaergaard Intrusion, East Greenland

		*Hawaiian lavas**					*Skaergaard Intrusion*						
	S	*Picrite basalt*	*Basalt*	*Andesine andesite*	*Oligoclase andesite*	*Soda trachyte*	*Gabbro picrite*†	*1st liquid (chilled marginal gabbro)*†	*2nd liquid*‡‡	*3rd liquid*‡‡	*4th liquid*‡‡	*5th liquid*‡‡	*6th liquid*‡‡
Be		—	—	—	—	8							
Ga	1	17	23	20	22	25	8	17	20	21	23	30	30
Cr	1	1700	470	—	—	20	1500	170	75	—	—	5	14
V	5	250	300	70	20	—	120	140	220	10	—	4	18
Mo	1	1	—	—	—	4	3	—	—	—	—	1	1
Li	1	1	2	15	20	30	2	2	4	5	7	17	13
Ni	2	1000	80	6	12	15	1000	170	50	—	—	5	8
Co	2	70	33	14	5	2	90	53	35	22	13	5	5
Cu	10	150	170	<10	<10	<10	100	130	220	360	440	260	20
Sc	10	—	10	—	—	—	—	12	15	9	8	2	—
Zr	10	70	100	350	1200	1500	30	50	80	90	180	550	850
Y	20	20	23	55	120	150	—	—	—	50	100	270	250
La	20	—	—	25	110	100	—	—	—	20	50	180	240
Sr	10	300	800	2500	3500	100	100	350	500	470	430	400	350
Ba	5	100	120	600	1000	800	10	45	90	170	230	630	1400
Rb	20	—	—	35	50	300	—	—	—	10	20	50	160

* Averages based on figures given in previous table.
† Quoted from Wager and Mitchell (1951, Table F, columns Y and A).
‡‡ Calculated values quoted from Wager and Mitchell (1951, Table 10, p. 174).

many of the common trace elements during fractionation has been commented on before (Wager and Mitchell, 1948); it will some day provide a powerful weapon for the solution of petrogenetic problems.

During the presumed, further crystal fractionation to give trachyte, it is found that the changes are in the same direction as for the earlier part of the series for most of the trace elements, namely, Ga, V, Li, Co, Zr, Y, La and Rb, and only in a different direction for Cr and Ni, both of which, rather surprisingly, increase slightly in amount, Sr, which decreases abruptly, and Ba, which decreases slightly.

The mugearite lavas of Skye (Harker, 1904; Kennedy, 1931; and Tilley, 1950, pp. 41–46) are rather similar to the andesine and oligoclase andesites of Hawaii. The mugearite H4098 from Skye forms the lower unit of a composite lava flow described by Harker (1904, pp. 259–63) and Kennedy (1931); it is similar in trace element composition to the andesine andesite of Hawaii, the only significant difference being in the relative abundance of Sr and Ba. The other mugearite analysed, H4096, is more leucocratic and resembles in trace element composition the oligoclase andesites. It is to be hoped that the current work of the Geological Survey will further define the variation in this group of Skye rocks.

The trace element status of the Skye trachyte H359 is not much different from the Hawaiian, except that V and Ba are higher. It would seem to represent a rather earlier stage in the differentiation series, at which Ba has not yet begun to decrease, but at which Sr has.

Comparison with the Skaergaard Intrusion

Trace element data on basic rocks are being accumulated rapidly as a result of the adoption of spectrographic techniques. Besides the older results from Goldschmidt and his co-workers (see Goldschmidt, 1937 for bibliography) there are published figures for basalts, dolerites or gabbros from North America generally (Sandell and Goldich, 1943), North America, Ontario, diabase (Fairbairn, Ahrens and Gorfinkle, 1953), Greenland (Wager and Mitchell, 1951), Sweden (Lundegardh, 1946), South Africa (Walker and Poldervaart, 1949), Scotland (Nockolds and Mitchell, 1948; Walker, Vincent and Mitchell, 1952), Northern Ireland (Patterson, 1951) etc. In a broad way the trace element content of basic rocks is known, but there are differences of a considerable size which may be due to (1) the limited accuracy of the analyses, (2) comparison being made of rocks at rather different stages in a crystal fraction series, (3) differences in the amount of contamination with surrounding rocks, (4) fundamental difference in the composition of basic magma in different regions of the Earth. At present it is likely that differences due to (1), (2) and (3) above are masking any fundamental regional difference, a point to which it is proposed to return in a subsequent paper.

Here it is proposed to compare the general trend shown by the Hawaiian rocks with that resulting from fractional crystallization of basic magma as exemplified by the Skaergaard intrusion, East Greenland. In the Skaergaard case direct observational data are only available for the successive crystal fractions but the trace element composition of the successive residual liquids has been estimated

indirectly (Wager and Mitchell, 1950). Comparing the Hawaiian and Skaergaard series (Table 2) and dealing only with the direction of change and not the absolute values, we may note:

Ga increases slightly in both series;
Cr decreases rapidly to very low values in both series but finally increases again slightly;
V increases slightly and then falls;
Mo occurs mainly in the earliest and latest fractions;
Li increases comparably in both series;
Ni decreases at first and then, after reaching a low value, slightly increases; this happens in both series, although it is reduced to a much lower level in the Skaergaard series;
Co decreases slowly but steadily in both series;
Cu shows a real difference in that it rises over a longer range and to much higher levels in the Skaergaard intrusion. It seems likely that the reason for this behaviour is connected with the contrasted volcanic and plutonic habits;
Sc shows in both series a maximum in the basic stage;
Zr increases steadily and rather rapidly in both series;
Y, La increase in both series;
Sr, in both series, increases at first and later decreases, but the changes are more emphatic in the Hawaiian sequence;
Ba, in both series, increases over most of the range but there is a slight fall in the latest Hawaiian rock which is not shown in the Skaergaard series;
Rb increases throughout in both series.

There is thus a close qualitative, and in many cases quantitative similarity in the trace element variation of the Hawaiian and Skaergaard series and this gives support for the view that both have resulted from the same process, which, on other grounds, is considered to be fractional crystallization. The similarities also increase the confidence which may be placed in the estimated trace element composition of the successive Skaergaard liquids, the composition of only the first, the original magma, being known by direct determination.

The amounts of original olivine basalt liquid which must have crystallized to yield the andesine andesite, oligoclase andesite and trachyte are estimated by Macdonald as 64, 70 and 86%, respectively (1949a, pp. 1575–6). If a trace element is wholly left behind in the residual liquid during fractionation then, when half the original liquid has crystallized, the amount of the element in the liquid will be doubled, when threequarters has crystallized, the amount will have increased four times and so on. Hyperbolic relationships of this sort for certain elements were obtained for the successive Skaergaard liquids over a considerable range (Wager and Mitchell, 1951, Fig. 7 and p. 177). If a small but roughly constant amount of the element is precipitated with the crystal phase the curve remains hyperbolic in form, but is displaced a uniform amount upwards. Of the trace elements determined in the Hawaiian lavas Zr, Y, La, Ba and Rb would be expected, on

the previous evidence (WAGER and MITCHELL, 1951, p. 176) to accumulate in the residual liquid in this way over the range considered. Thus, while 64, 70 and 86% of the original basalt magma crystallized to give, by fractionation, the andesine andesite, oligoclase andesite and trachyte respectively, there should be an increase of 3, $3\frac{1}{2}$ and 7 times in the amounts of these particular elements; the spectrographic results indicate increases of this order or more.

REFERENCES

AHRENS, L. H. (1951) *in* Co-operative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks. U.S. Geol. Survey Bulletin 980

DALY, R. A. (1944) Volcanism and petrogenesis as illustrated in the Hawaiian Islands. Bull. Geol. Soc. Amer. **55**, 1363–1400

FAIRBAIRN, H. W., AHRENS, L. H. and GORFINKLE, L. G. (1953) Minor element content of Ontario diabase. Geochim. et Cosmochim. Acta, **1**, 34

GOLDSCHMIDT, V. M. (1937) The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. for 1937, 655–673

HARKER, A. (1904) Tertiary igneous rocks of Skye. Mem. Geol. Surv. Great Britain

KENNEDY, W. Q. (1931) On composite lava flows. Geol. Mag. **68**, 166–181

LUNDEGARDH, P. H. (1946) Rock composition and development in Central Roslagen, Sweden. K. Svenska Vetenskapsakademien. Arkiv. Kemi. Mineral. Geol. **23A** (No. 9) 1–160.

MACDONALD, G. A. (1949a) Hawaiian petrographic province. Bull. Geol. Soc. Amer. **60**, 1541–1596

MACDONALD, G. A. (1949b) Petrography of the Island of Hawaii. U.S. Geol. Surv. Professional Paper 214-D

NOCKOLDS, S. R. and MITCHELL, R. L. (1948) The geochemistry of some Caledonian plutonic rocks; a study in the relationship between the major and trace elements of igneous rocks and their minerals. Trans. Roy. Soc. Edinburgh **61**, 535–575

PATTERSON, E. M. (1951) A petrochemical study of the Tertiary lavas of north-east Ireland. Geochim. et Cosmochim. Acta **2**, 283–299

SANDELL, E. B. and GOLDICH, S. S. (1943) The rarer metallic constituents of some American igneous rocks. J. Geol. **51**, 99–115 and 167–189

STEARNS, H. T. and MACDONALD, G. A. (1946) Geology and ground-water resources of the Island of Hawaii. Hawaii Division of Hydrography Bull. 9

TILLEY, C. E. (1950) Some aspects of magmatic evolution. Quart. Journ. Geol. Soc., **106**, 37–61.

WAGER, L. R. and MITCHELL, R. L. (1948) The distribution of Cr, V, Ni, Co and Cu during the fractional crystallization of a basic magma. Internat. Geol. Congr. Report of the 18th Session, Great Britain, 1948, Part II

WAGER, L. R. and MITCHELL, R. L. (1951) The distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland. Geochim. et Cosmochim. Acta **1**, 129–208

WALKER, F. and POLDERVAART, A. (1949) Karroo dolerites of the Union of South Africa. Bull. Geol. Soc. Amer. **60**, 591–706

WALKER, F., VINCENT, H. C. G. and MITCHELL, R. L. (1952) The chemistry and mineralogy of the Kinkell tholeiite, Stirlingshire. Min. Mag. **29**, 895–908

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Natural variations in the isotopic constitution of silicon

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ABSTRACT

The isotopic constitution of silicon in minerals and rocks has been examined. In general, the Si^{30} content decreases as one goes from a high-temperature mineral (olivine) to low-temperature pegmatite quartz to vein quartz to geyserite; the greatest isotope separation occurring in the last two steps, which involve deposition from an aqueous phase rather than crystallization from a silicate melt. Organic silica deposited from sea-water (chert, marine diatomite) shows an increase in Si^{30} over olivine, whereas a fresh-water diatomite has an isotopic composition consistent with that of silicon from hot springs (geyserite). The isotopic composition of silicon in a stony meteorite is surprising, as it shows a lower Si^{30}/Si^{28} ratio than olivine or even oligoclase from a pegmatite. In general the distribution of the silicon isotopes is similar to that of oxygen isotopes reported by SILVERMAN; some exceptions are noted. The variation in isotopic constitution of silicon is small (the maximum difference encountered in the ratio Si^{30}/Si^{28} being 3 *per mil*) indicating presumably a relatively simple geochemical history involving few opportunities for exchange with gas phases or aqueous solutions.

1. INTRODUCTION

The purpose of the work described in this paper was to make a preliminary survey of the variations in the isotopic constitution of silicon from minerals and rocks. That such variations would be small was apparent from the outset for reasons given below; yet it was felt that even subtle variations, if any, might be used to advantage in determining the relative temperature of crystallization of silicate minerals, or to determine whether any particular rock formed from a silicate melt or from an aqueous solution, or to trace in general the geochemical history of silicon. To test the existence of systematic variations with temperature of crystallization, a sequence of minerals was selected, ranging from olivine (high temperature) to quartz and oligoclase from a pegmatite. To demonstrate systematic variations resulting from the mode of formation, we included vein quartz, a deposit from hot springs (geyserite), and marine sediments of organic, or partly organic, origin (chert, diatomite). Results given in this paper indicate that further studies in this field would not be unprofitable.

2. EXPERIMENTAL METHOD

The experimental part of this survey consisted, briefly, in converting the silicon from various minerals into gaseous SiF_4 and assaying this gas for isotopic constitution in a mass spectrometer recently erected at the University of California, Berkeley. If an experimental programme of this type is to be successful, there are two requirements which must be fully satisfied:

(i) There must be available a chemical procedure for converting the silicon in a mineral specimen to a test sample the composition of which is in unique and fixed correspondence with the isotopic constitution of the original mineral specimen.

(ii) There must be available a mass spectrometer procedure for assaying the test sample with a precision high enough so that uncertainties in the assay are appreciably smaller than the isotopic variations encountered.

It will be profitable to discuss the experimental methods finally adopted as they bear upon one or the other of these requirements.

A. *The chemical conversion*

For the conversion to meet the requirement of *unique* correspondence between mineral specimen and test sample, the only positive technique is one which has 100% chemical yield. Thus considerable effort was directed toward developing a high yield procedure. The conversion must also evolve a test sample which is uniformly free from chemical impurities which would contribute ions of the same mass as those measured in the spectrometer. For the correspondence to be *fixed*, the test sample must be stable and, of great importance in a silicon investigation, must not exchange silicon with its surroundings.

Accordingly, the test samples used throughout this investigation were precipitated barium fluosilicate, $BaSiF_6$. This compounds is a white solid which can be prepared in a pure state, dried, and stored indefinitely without deterioration. Upon heating in vacuum it decomposes, however, to solid BaF_2 and gaseous SiF_4, which latter serves as the source of the SiF_3^+ ions observed with the mass spectrometer.

The first chemical step is to convert the silicon in the mineral specimen to SiO_2 by one of the standard analytical procedures (Hillebrand and Lundell, 1929) which have been well tested geochemically for quantitative yields of pure silica. Next, an intimate mixture of 0·5 grams of this silica and 2·5 grams of sodium carbonate is fused in a 20 ml platinum crucible to give a clear melt. Upon cooling, the solidified melt may be extracted as a pellet by pressing the crucible gently around the base. This pellet dissolves in 15 ml of water to give a clear solution. To this is added 30 ml of concentrated perchloric acid and the solution is heated on the hot plate, swirling constantly by machine to avoid bumping, until copious dense fumes of perchloric acid have come off for ten minutes. When cooled, the solution solidifies to a gelatinous mass which is then taken up in 200 ml of water, brought to a boil (again swirling!) and the precipitate of gelatinous silica filtered and transferred to a polyethylene beaker with 60 ml of water. Concentrated HF is added dropwise until the solution just clears upon total conversion of the silica gel to fluosilicic acid, H_2SiF_6. To the clear solution is added 20 ml of a solution containing 0·2 grams of $BaCl_2 \cdot 2H_2O$ per ml. Under these conditions $BaSiF_6$ precipitates while BaF_2 does not. For complete precipitation, the beaker is allowed to stand overnight before filtering and drying the $BaSiF_6$ at 110°C.

The above procedure was subjected to a series of analytical tests in order to determine the chemical yield. A typical test consisted in starting with a weighed amount of silica, precipitating $BaSiF_6$ with a calibrated barium solution, weighing the precipitate, and extracting and weighing the unreacted barium in the filtrate as $BaSO_4$. Within the accuracy of these tests (2%) the following facts were established:

(i) $BaSiF_6$ is a correct formula representation of the barium chloride precipitate when the above procedure is adhered to strictly. Thus, occluded water and coprecipitated BaF_2 are not present in weighable amounts.

(ii) The yield of $BaSiF_6$ always exceeds 95% of the theoretical yield calculated from the amount of input silica.

This yield was considered completely satisfactory for the research. The final step preceding the mass spectrometry is to weigh out 150 mg of the dried test material into a short length of 10 mm pyrex tubing, closed at one end. This tube is sealed to a 75 ml pyrex sample bulb fitted with a stopcock. The bulb is evacuated with a diffusion pump for 12 hours or more, flaming gently from time to time in order to facilitate the removal of water vapour. Then with stopcock closed, the $BaSiF_6$ is decomposed by heating the bottom of the 10 mm tube vigorously with an oxygen-gas flame until there is no further visible change in the solid material. The temperature of the glass is brought to such a point in this heating that the glass softens and begins to collapse around the solid BaF_2 residue. Lastly, the lower half of the 10 mm tube is sealed off with the torch from the rest of the sample bulb so as to remove the BaF_2 residue and prevent any recombination which might be isotopically selective. Control experiments show that the percentage decomposition of the $BaSiF_6$ by this scheme is 90%. (For 100% decomposition the solid must be heated to a higher temperature than is possible in a "Pyrex" system.)

Involving as it does, silicon in both gas and solid phases, this 10% incomplete thermal decomposition of $BaSiF_6$ was viewed as a potential source of isotope fractionation. Accordingly careful checks were made to verify that the procedure is satisfactory. Thus samples of the same $BaSiF_6$ were decomposed by mild heating in "Pyrex," by vigorous heating in "Pyrex," and by maximal heating in fused quartz—in each case with and without the prior, prolonged, 12-hour evacuation. Isotope measurements made on the six gas samples so obtained were indistinguishable.

As regards purity of the test material, the criterion for acceptability is simply that there must not be evolved with the SiF_4 a volatile companion which contributes ion peaks at the mass positions under scrutiny, namely 85, 86, and 87. As far as could be established by scrutiny of the change in ion background, upon introduction of the sample into the mass spectrometer, at mass positions adjacent to these, there were no such impurity peaks present. (The no-sample ion background at masses 85, 86, and 87 was extraordinarily low after baking the source region of the mass spectrometer—a precaution which was always exercised. Referred to the sample-in intensity at these positions, these backgrounds were 0·004, 0·04 and 0·03 *per mil* respectively. These could be observed only by operating the spectrometer at a sensitivity 200 times that employed in taking data at masses 86 and 87 with sample in!) Adjacent mass positions were scrutinized for spurious sample ions as routine procedure at the time of each run. Occasionally the entire mass spectrum from mass 12 to mass 150 was examined for impurity ions. Except for SiF_4 ions of the type $Si_xF_y^{z+}$, where x, y, and z are small integers, the only spurious ions ever observed in association with the sample were those which could be attributed to small concentrations of water in the sample. These were O^+, OH^+, H_2O^+, HF^+, SiF_2O^+, SiF_2HO^+, and $SiF_2H_2O^+$. These last three, while

small, have principal ions at masses 82, 83, and 84 and were at first a source of concern since it was recognized that isotopic ions of these could contribute to the spectrum at masses 85, 86, and 87. For example, there would be contributions at mass 87 due to $Si^{29}F_2H_2O^{18+}$ and $Si^{30}F_2HO^{18+}$. However, in the worst case seen these would influence the measured Si^{30}/Si^{28} ratio by only 0·02 per mil, an effect which is completely negligible.

Lastly as regards impurities, we were always mindful of the possibility of a hydride impurity ion SiF_3H^+. This ion if present would have the disastrous effect of superposing an 86, 87, 88 spectrum upon the primary one in a strength which would doubtless vary from sample to sample. Fortunately, there was never any evidence that this ion occurs. Its presence would be betrayed by changes in the background at mass 88 and by large fluctuations in the 86/85 ratio (amplified here because Si^{28}/Si^{29} exceeds $Si^{29}/^{30}$ by a factor of 13). Both of these effects were looked for but never found.

Selection of $BaSiF_6$ as the test material greatly simplifies the problems of stability and exchange, which are conveniently discussed together. The compound can be prepared entirely by "wet" chemistry and the use of platinum and polyethylene vessels at appropriate stages in the procedure excludes the possibility of contamination. As mentioned earlier, $BaSiF_6$ can be stored indefinitely without deterioration. Prior to the actual measurement, however, the compound is decomposed in an evacuated glass bulb to produce SiF_4, which gas is stored (in some cases for appreciable times) in the glass bulb, is admitted to the glass sample system of the mass spectrometer, and is finally leaked into the source region—largely of glass construction—of the mass spectrometer itself. If water vapor could be excluded entirely from all these steps, there would be no question as to the stability of the sample gas and the absence of exchange. Complete exclusion of water was not found to be practical, however, and as evidenced by the impurity spectrum discussed above, water vapour was always present in trace amounts. Accordingly we can expect that to some degree the reaction

$$SiF_4 + 2H_2O \rightarrow SiO_2 + 4HF$$

will occur and there can be a subsequent reverse reaction between HF and the glass surroundings:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

The net effect of this process is, of course, to substitute silicon from the laboratory glassware for the original silicon of mineral origin.

To determine unambiguously the magnitude of this effect, a sample of silica was artificially enriched in Si^{29} by adding 1·10 mg of enriched $Si^{29}O_2$ to 234 mg of normal silica. From the known isotopic constitution of these, it was possible to calculate that the Si^{29} content of the mixture was 66·3 per mil in excess of that in normal material. The mixed silica was then converted to $BaSiF_6$ by the procedure discussed above. When SiF_4 was evolved and measured in the usual way, the observed Si^{29} was in excess of that observed in normal material by 64·8 *per mil*. The degree of exchange as measured by this single experiment was thus 2·3%.

This exchange, if real, does not affect the measurements reported in this paper by a detectable amount since the Si^{30}/Si^{28} never differs from that of the glassware by more than 2 per mil. The Si^{29} enriched gas sample was re-examined for isotopic constitution after having been stored in the glass sample bulb for 75 days. No additional exchange was found.

This very abnormal sample was also useful in searching for "memory" effects in the mass spectrometry. It was found by running the abnormal gas and normal samples consecutively that, if our standard procedure for sample change was employed, the measured isotopic constitution of a given gas sample was independent of previous sample history.

B. *The mass spectrometry*

The abundance ratio Si^{30}/Si^{28} was measured for the various samples by admitting SiF_4 to a 9-inch radius, 60° deflection, Nier type (NIER, 1940) mass spectrometer of conventional design and by collecting the ions $Si^{28}F_3^+$ and $Si^{30}F_3^+$ *singly*. There is no question but what *dual* collection of these ions would comprise a better technique for this study, but the Berkeley spectrometer, designed for a variety of applications, has not been adapted for this technique. It was felt, moreover, that by exercising certain precautions in the spectrometry sufficient precision would be obtainable to meet the needs of this survey. This proved to be the case: the average deviation in the measured Si^{30}/Si^{28} ratios for the SiF_4 evolved from a given mineral sample was 0·35 per mil.

Since the techniques for making isotopic measurements from gas samples with routine precision (perhaps 5 per mil) are well described in the literature (INGHRAM, 1948), this discussion is limited to those points in the procedure which, in the opinion of the authors, are essential to obtaining the increased precision quoted.

Foremost among these points was adjustment of the spectrometer to give completely resolved but "flat-topped" ion peaks. Magnetic sweep was employed and was adjusted so that the full ion current (corresponding to the flat top) for a given mass position was collected for at least eight seconds on each sweep. This allowed adequate time for the recording system, of time constant 0·5 seconds, to respond to the ion signal. To ensure further that there would be no time discrimination in recording ion currents, the magnet was always recycled to a mass position 6 mass units distant from the first position recorded, so as to eliminate hysteresis effects in the sweep rate characteristic. This could be accomplished without delay by sweeping over the intervening positions at a higher speed.

The recording system included a 5×10^{10} ohm Victoreen resistor, an Applied Physics Corp. vibrating reed electrometer, and a Brown strip chart recording potentiometer. This system provides exceptional stability, virtually no zero drift, and low noise. The peaks at masses 86 and 87 were recorded at 20 times the sensitivity at mass 85. This sensitivity change was accomplished with a constant input impedance voltage divider in the output circuit of the electrometer. This ensured that the electrometer saw no circuit changes, contributing to stability. The source impedance for the Brown potentiometer was switched from 10 ohms to 200 ohms in this procedure, but the instrument is not sensitive to impedance

changes in this range. The gain of the Brown potentiometer must be checked periodically however: if low, the instrument may not respond to within one slidewire convolution on the low sensitivity setting; if high, the instrument may fluctuate excessively on the high sensitivity setting.

The critical elements in the sample system were a 300 ml pyrex sample bulb followed by a pin-hole leak consisting of a 0·001 inch diameter hole in an aluminium foil 0·001 inches thick. The pressure of SiF_4 in the sample bulb was 50 microns and was constant from sample to sample within 15%. (Variations in sample pressure were always compensated by adjustment of the ionizing electron current so that peak deflections were a uniform fraction of chart width.) The conditions for molecular flow through the leak are rigorously fulfilled for these pressures and hole size so that there is no possible variation in abundance ratio with the quoted variations in sample pressure. Change, due to molecular flow, in isotopic constitution in the sample bulb was completely negligible within the 20 minutes required for a single assay of ten complete sweeps. The period for sample exhaust was arbitrarily set at 15 minutes, bringing the period of the complete measuring sequence to about 40 minutes.

The ion source used in this study was of standard design except for minor changes in physical construction necessitated by the use of 4500 volts accelerating potential. The electron current was regulated electronically to better than 1 part in 2000. No auxiliary magnet was used to align the electron beam.

Values of the Si^{30}/Si^{28} ratio in this survey are referred to that for a standard silicon (from N.C. olivine), a measurement of the latter always being interposed between two separate runs on the unknown material. It was very gratifying to observe that there were no long term or short term variations in the abundance ratio for the standard silicon. Deviations in this quantity were simply statistical fluctuations about a static mean.

3. Experimental Results

The Si^{30} Si^{28} ratios for the various samples are referred to that for our standard silicon from olivine, $(Si^{30}/Si^{28})_0$, by evaluating the customary quantity

$$\delta \equiv 1000 \cdot \frac{(Si^{30}/Si^{28}) - (Si^{30}/Si^{28})_0}{(Si^{30}/Si^{28})_0}$$

which expresses in per mil the degree by which Si^{30} was found to be in excess. Table 1 presents values of δ for 14 mineral specimens, summarizing the results of 39 separate determinations of the abundance ratio, each comprising 10 distinct measurements.

Probable errors were computed both on the basis of internal consistency of the single measurements and external consistency of the separate determinations. These are, on the average, in good agreement suggesting that any systematic errors in the measurement of the Si^{30}/Si^{28} ratios were constant and thus cancelled out in the calculation of S. The probable error quoted in Table 1 is always the larger of the two, however.

It is unfortunate that a large body of careful data, namely 83 separate determinations, each comprising again 10 distinct measurements, could not be included

Table 1. *Variations in per mil of the abundance ratio* Si^{30}/Si^{28} *referred to that for silicon from olivine*

Sample No.	*Description*	δ *in* ‰	*No. of determinations*	*Prob. error in* ‰
2	Chert, partly recrystallized, Franciscan (Jurassic?), California	+1·0	2	0·3
17	Marine diatomite, Miocene, Santa Barbara, California	+1·0	2	0·4
14	Chert, Monterey formation (Miocene), Berkeley, California	+0·5	2	0·2
1	Olivine (90% forsterite) from dunite, Jackson Co., North Carolina	0·0	13	—
5	Quartz, from pegmatite, Topaz Lake, California	−0·1	2	0·2
6	Oligoclase (24% An) from pegmatite, Topaz Lake, California	−0·4	2	0·3
18	St. Peter Sandstone, Cambrian, Beloit, Winsconsin	−0·4	2	0·3
7	Augite, from picrite basalt tuff, Mauna Kea, Hawaii	−0·7	2	0·4
13	Stony meteorite, Melrose, New Mexico	−1·0	2	0·3
3	Vein quartz, well crystallized, Hot Springs, Arkansas	−1·1	2	0·2
4	Biotite, from pegmatite, Topaz Lake, California	−1·5	2	0·2
12	Diatomite, fresh water, California	−1·6	2	0·2
16	Flint, from Dover chalk	−1·8	2	0·3
15	Geyserite, Yellowstone	−2·1	2	0·5

with this compilation. These particular data were obtained with samples of $BaSiF_6$ prepared by an earlier chemical procedure, differing from that described above in that SiO_2 was converted to silica gel by a step involving the evolution of SiF_4 gas. Although the results of these early measurements were in substantial agreement with those reported in Table 1, there were two samples of $BaSiF_6$ which gave values of δ much in excess of the maximum value 1·0 found there. These two, while highly reproducible for gas samples prepared from the $BaSiF_6$ in question, could not be reproduced for other samples of $BaSiF_6$ prepared from the same mineral. This fact pointed to at least occasional isotope fractionation in the

chemical conversion, which by the early method was not of uniform, high, chemical yield. Accordingly, the chemistry was revised and the early results discarded. We emphasize, however, that these data, obtained with a totally distinct series of test samples, lend support on the whole to the reality of the variations tabulated in Table 1.

4. Discussion of Results

Although the number of specimens studied in this investigation is too small to warrant any generalization, attention may be called to certain features of the present results which may be significant. In the first place, the differences recorded here are small, the maximum deviation between extreme compositions being about 3‰. The corresponding range for oxygen in silicates, according to Silverman (1951) is 33‰. Such a difference between these two elements was not entirely unexpected, one reason for it being the difference in mass ratios (30/28 = 1·07 for silicon, as against 18/16 = 1·125 for oxygen). Yet Thode (1949) has found large differences in sulphur (34/32 = 1·06), and large differences in the ratio C^{13}/C^{12} (mass ratio = 1·08) in carbonates have been reported by Baertschi (1951).

Isotopic separation being a non-classical effect, one might also expect a relatively small fractionation in silicates because of their relatively high temperature of formation. Yet Silverman finds significant differences in the oxygen ratios in these same silicates. It should be kept in mind also that "high temperature" means essentially a temperature that is high in comparison to some characteristic temperature of the mineral. As silicates usually have a Debye temperature of several hundred degrees K, one might still expect to find in silicates fractionation coefficients similar to those found by Baertschi for carbonates formed at lower temperatures.

It is well known that separation of isotopes in reactions involving different phases (e.g., liquid-gas) will depend on the relative number of degrees of freedom of the isotopic molecule in the two phases (see Waldman, 1943). One would therefore not expect a large fractionation in processes involving straightforward crystallization of silicates from corresponding silicate melts, as many of the characteristic structural features of the solid phase presumably exist also in the liquid (SiO_4 groups, chains, etc.). Yet one would expect some fractionation in processes involving aqueous solutions or gas phases; and it was indeed observed, as reported above, that fractionation of the silicon isotopes may occur in some laboratory reactions by which silicon in silicates is converted to silicon tetrafluoride. This fractionation would, in general, lead to enrichment of the light isotope in the gaseous phase. In agreement with this expectation, it was found that the "lightest" of all samples examined so far is the geyserite No. 15, geyserite being a hot-spring deposit undoubtedly formed from silica carried in an aqueous vapor phase. Keeping this in mind, the relatively small difference between olivine on one hand, and quartz and oligoclase from a pegmatite on the other, would appear to indicate that the latter minerals formed through a relatively simple process of direct crystallization. The difference between the pegmatite quartz No. 5 and the vein quartz No. 3 is again in agreement with the hydrothermal origin of the latter. It is worth noting that the difference between quartz and oligoclase

in the same pegmatite is in the same direction as the similar difference in oxygen ratios in quartz and potash feldspar from pegmatite reported by SILVERMAN; the heavier isotope going selectively into quartz in preference to feldspar. The rather striking difference in isotopic composition of silicon in biotite (No. 4) in the same pegmatite might indicate that the biotite formed from an aqueous phase rather than by direct crystallization from a silicate melt.

The small increase in Si^{28} in pegmatite quartz and oligoclase as compared with olivine from a dunite may also be indicative of a gradual increase in the proportion of the lighter isotope in minerals crystallizing from a melt at gradually decreasing temperatures. One would indeed expect a silicate containing a higher proportion of the lighter element to have a lower melting point, a higher vapour pressure, etc. The difference, however, is small. If an effective fractionation of isotopes is an indication of the operation of a gas phase, then the rather large difference between olivine from dunite (No. 1) and a stony meteorite (No. 13) is surprising. It is usually believed that dunites and the more common peridotites represent either fragments of an undifferentiated mantle with the gross composition of meteorites, which have been squeezed up mechanically, or, alternatively, that they result from remelting and crystallization of portions of this same mantle. In either case the isotopic composition should not be very different from that of the parent material, as olivine (dominantly forsterite) crystallizes at such high temperatures that little isotopic separation would be expected. It is also puzzling that SILVERMAN finds no significant difference in the oxygen ratios in stony meteorites and dunites; for it is difficult to see how separation of silicon isotopes could occur without simultaneous fractionation of oxygen isotopes. One would thus venture to say that either the present results are not representative, or that silicon in dunites has a more complicated history than previously suspected.

Turning now to sedimentary rocks, it may be recalled that Silverman observed a gradual increase in the amount of heavy oxygen with increasing amounts of secondary silica, that is, of silica deposited from sea water. For instance, the St. Peter Sandstone, which is uncemented, has an O^{18}/O^{16} ratio which is not very different from that of average igneous rock; a quartzite with 20% secondary silica is somewhat higher in O^{18}; a flint from the Dover chalk, and a marine diatomite from Santa Barbara, both of which consist entirely of secondary silica (much of which may, of course, be of organic origin), also contain a much higher proportion of the heavy isotope of oxygen. SILVERMAN believes that this enrichment in O^{18} results from an exchange reaction with sea water which becomes correspondingly enriched in O^{16}, as it is found to be.

Examining present results for silicon, we may note first that the isotopic composition of the St. Peter Sandstone (No. 18) is not significantly different from that of the average for pegmatite quartz (No. 5) and vein quartz (No. 3), or from that for oligoclase (No. 6). This agrees with SILVERMAN's finding. The Franciscan (Jurassic?) and Monterey (Miocene) cherts, and the Santa Barbara diatomite (No. 17) show a marked increase in the heavy silicon isotope, again in agreement with SILVERMAN's results for oxygen. Yet it is difficult to believe that this enrichment in Si^{30} could have the same origin as the enrichment in O^{18} since the amount of silicon in sea water is extremely small, of the order of 4g/ton, as against 89% for

oxygen. If there were an exchange reaction leading to an enrichment of Si^{30} in all sediments, as SILVERMAN assumes to be the case for oxygen, one wonders where the corresponding amount of Si^{28} would be stored. Since the cherts and diatomite are probably largely if not entirely of organic origin, it may be that their isotopic enrichment is due to selective organic processes, and is therefore restricted to the relatively small volume of sediments of organic origin. If this be the case for silicon, it might also be the case for oxygen, and the enrichment in O^{18} in sediments might be partly due to causes other than exchange with water.

The diatomite No. 12 shows, in contrast to the marine diatomite No. 17, a marked enrichment in Si^{28}. This diatomite No. 2 is, however, of fresh-water origin, and its isotopic composition would be strongly influenced by that of the silicon in the relatively small body of water in which it accumulated. Common association of fresh-water diatomites and lavas has led to the hypothesis, which is usually accepted by geologists, that the silica entering into the diatomite is supplied directly from hot springs or other volcanic sources: this view is well supported by the composition of the hot-spring geyserite No. 15.

Present results for chert No. 16, from the Dover chalk, stand in sharp contrast to SILVERMAN'S results for oxygen in this same rock. No explanation of this discrepancy is available at present.

Recapitulating, this investigation reveals the existence of small variations (about 3‰) in the isotopic composition of silicon in various minerals and rocks. Such variations appear to be related to the mode of formation of the rock, marine sediments of organic origin (chert, diatomite) showing an increase in the proportion of Si^{30} over silicate minerals from igneous rocks, whereas silica deposited from an aqueous phase (vein quartz, geyserite) contains, as expected, more of the lighter isotope. Among the minerals from igneous rocks, the trend is, again as expected, towards enrichment in Si^{28} in the low temperature minerals of a pegmatite, in which the heavy isotope of silicon shows a slight preference for quartz rather than feldspar, as is the case also for oxygen. The high content of Si^{28} in biotite from this same pegmatite may indicate intervention of an aqueous phase rather than simple crystallization from a silicate melt. The enrichment in Si^{30} in organic sediments is tentatively ascribed to selective organic action.

The present investigation also reveals certain unexplained differences in the distribution of silicon and oxygen isotopes. For instance, a flint from the Dover chalk is enriched in the light silicon isotopes as well as in heavy oxygen. Olivine from dunite shows more Si^{30} than a stony meteorite, which has an almost identical O^{18}/O^{16} ratio.

The variations in the isotopic composition of silicon observed so far are considerably smaller than those reported previously for carbon, although the mass ratio C_{13}/C_{12} is not significantly different from the mass ratio Si^{30}/Si^{28}. This is believed to be due essentially to the absence of such massive concentrations of Si in aqueous solution or gas phases (ocean, atmosphere) as occur in the elements carbon and oxygen; the geochemical history of silicon in the samples studied is apparently a rather simple one, involving mainly crystallization from melts and offering relatively fewer opportunities for exchange between solids and gases or aqueous solutions than is the case for oxygen or carbon.

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REFERENCES

BAERTSCHI, P.	1951	Relative abundance of oxygen and carbon isotpoes in carbonate rocks. Nature. **168**, 288–9
HILLEBRAND, W. F. and LUNDELL, G. E. F.	1929	Applied Inorganic Analysis, p. 714. Wiley, New York
INGHRAM, M.G.	1948	Modern Mass Spectroscopy. Advances in Electronics, Vol. I, p. 219. Academic Press, New York
NIER, A. O. C.	1940	A mass spectrometer for routine isotope abundance measurements. Rev. Sci. Instrum., **11**, 212
SILVERMAN, S. R.	1951	The isotope geology of oxygen. Geochim. et Cosmochim. Acta. **2**, 26–42
THODE, H. G.	1949	Variations in abundances of isotopes in nature, Research, **2**, 154–61
WALDMAN, L.	1943	Zur Theorie der Isotopentrennung durch Austauschreaktionen. Naturwiss., **31**, 205–6

Geochimica et Cosmochimica Acta, 1953, Vol. 3, pp. 235 to 243. Pergamon Press Ltd., London

Sulphur isotope fractionation in nature and geological and biological time scales*

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ABSTRACT

The sulphur isotope content of marine sulphide and sulphate deposits, as found in limestone and shales covering a wide range of geological ages, has been investigated. The results indicate a striking correlation between geological age and isotopic content, particularly for the sulphides. It would appear that isotopic fractionation began about 700–800 million years ago and that since then the sulphides have been depleted and the sulphates enriched in the heavy isotopes of sulphur. The maximum spread in the S^{32}/S^{34} ratio at the present time is about 7% or about the fractionation expected, if the most favoured distribution (thermodynamic-equilibrium) of S^{34} were established between $SO_4^=$ and H_2S. It seems fairly certain that the biological sulphur cycle in nature provides a mechanism for the exchange of the sulphur isotopes between $SO_4^=$ and H_2S. The results indicate that autotrophic organisms, which oxidize H_2S, did not become significant before 700–800 million years ago.

Introduction

Previous work has shown that marked variations in the abundances of the sulphur isotopes occur in samples of terrestrial origin (Thode *et al.*, 1948 and 1949; Trafimov, 1949; Szabo *et al.*, 1950; Macnamara and Thode, 1950; Tudge and Thode, 1950; Macnamara, 1951; Thode *et al.*, 1951; Macnamara and Thode, 1951; Macnamara *et al.*, 1952). Variations up to 4 and 8% have been found in the S^{33} and S^{34}, respectively. This would indicate a maximum spread of 16% in the S^{36} content. In general, sulphates are enriched and sulphides depleted in the heavy isotopes of sulphur (see Fig. 1). Pyrites extend over the middle range of isotope concentration and sulphur of organic origin tends to be low in the heavy isotopes. Meteoritic sulphur on the other hand has been found to have a constant ratio (Macnamara and Thode, 1950), about in the middle of the spread for terrestrial samples and close to the values obtained for sulphur of igneous origin. Macnamara and Thode (1950) have suggested that initially terrestrial sulphur was identical in isotopic content with meteoritic sulphur, and that since then isotopic fractionation has occurred above and below this base level through biological and geological processes. More recent investigations (Macnamara *et al.*, 1952) show small variations between meteoritic and igneous rock sulphur.

It is clear that the isotopes of sulphur do differ in their chemical properties and that fractionation can occur in chemical reactions both in nature and in the laboratory. Using the methods of statistical mechanics Tudge and Thode (1950) have calculated exchange constants for many possible exchange reactions of the sulphur isotopes. These calculations show that fractionation of the sulphur isotopes can take place in chemical reactions and that variations in the S^{34} content up to about 8% can be expected. For example, for the reaction

$$H_2S^{34} + S^{32}O_4^= \text{ sol.} \rightleftharpoons H_2S^{32} + S^{34}O_4^= \text{ sol.} \qquad (a)$$

* Presented at the A.C.S. meeting, New York City, September 1951, also at a Mass Spectrometer Symposium, Bureau of Standards, Washington, September 1951.

the equilibrium constant is calculated to be 1·074 at 25°C. This means that S^{34} should be favoured in the sulphate ion by about 7·5% under equilibrium conditions. This is about equal to the overall spread found in the isotopic ratio between sulphides and sulphates occurring naturally. Szabo, Tudge, Macnamara and Thode (1950) have pointed out that isotope exchange between sulphates and sulphides, according to Reaction (*a*) could take place through the well-known sulphur cycle in the sea (see Fig. 2). In this cycle, sulphate is continually being reduced, either by bacterial reduction under anaerobic conditions or through plant metabolism of $SO_4^=$ and finally by bacterial reduction under anaerobic conditions or through plant metabolism of $SO_4^=$ and finally by bacterial reduction of organic

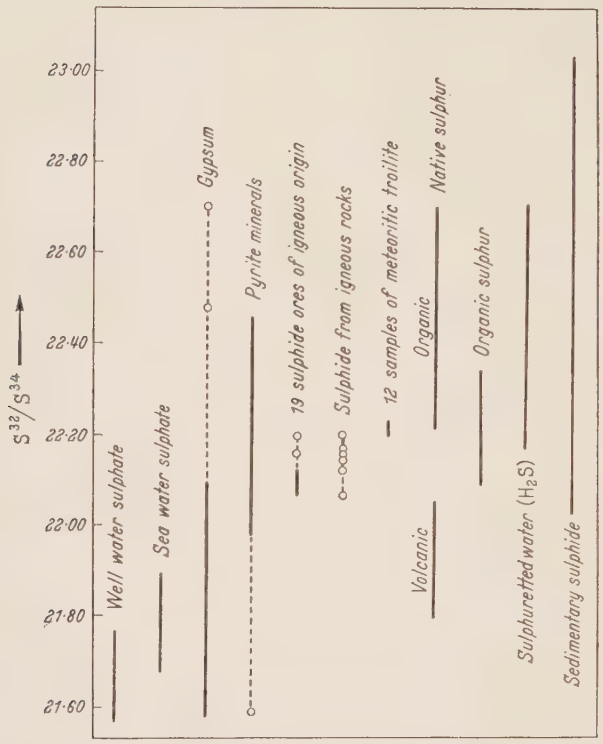

Fig. 1. The distribution of S^{34} in terrestrial and meteoritic sulphur*

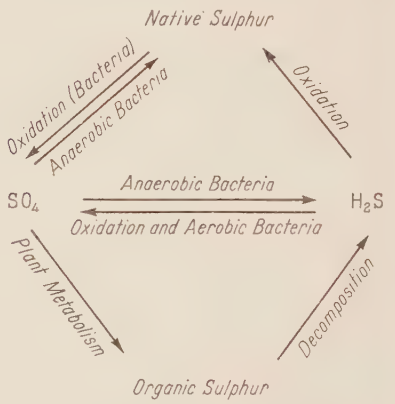

Fig. 2. The biological sulphur cycle

matter to H_2S. At the same time sulphides and H_2S are being oxidized mainly by bacterial action to free sulphur and finally sulphate or to sulphate directly. Some evidence that this cycle is responsible for the sulphur isotope fractionation found has already been reported. Thode, Kleerekoper and McElcheran (1951) found that $SO_4^=$ reducing bacteria, Vibrio desulphuricans, produce H_2S depleted in S^{34} compared to the $SO_4^=$ medium. Further, Macnamara and Thode (1951) showed that free sulphur produced in the bottom of lakes from sulphate by bacterial action contained 3·2% less S^{34} than the sulphate from which it was produced.

The question arises as to how long these processes have been going on, and to what extent has the sulphur cycle maintained or produced isotopic equilibrium

* A more accurate investigation of sea water sulphates has just been completed and shows an average value of 21·8 with a much smaller spread than is indicated in Fig. 1 and Fig. 3.

between sulphates and sulphides. To answer these questions samples of sulphides deposited from the sea at different periods in geological time as found in sedimentary rocks, have been studied. Also sulphates in limestone rocks of known ages have been investigated. The results of these isotopic studies are reported in this paper.

Experimental

Mass spectrometry

The relative abundances of the sulphur isotopes were obtained with a 180° directional focusing mass spectrometer of the Nier type (Thode *et al.*, 1945). A vibrating reed D.C. amplifier together with a *Leeds & Northrup* speedomax recorder were used to measure the isotopic abundances. The mass spectrometer tube and electronic units have been described previously (Lossing *et al.*, 1947; Graham *et al.*, 1947).

Sulphur dioxide was chosen as the best gas for mass spectrometer studies of the sulphur isotopes. The S^{32}/S^{34} ratio as determined from the SO_2^+ ions may be calculated directly from the mass spectrometer ratio of mass 64 to 66. The $S^{32}O^{17}O^{17}$ and $S^{33}O^{16}O^{17}$ species are of such small abundance that their contribution to the 66 peak height may be neglected.

$$\frac{64}{66} = \frac{S^{32}O^{16}O^{16}}{S^{34}O^{16}O^{16} + S^{32}O^{16}O^{18}} = \frac{1}{2\dfrac{O^{18}}{O^{16}} + \dfrac{S^{34}}{S^{32}}}$$

Thus

$$\frac{S^{32}}{S^{34}} = \frac{1}{\dfrac{66}{64} - 2\dfrac{O^{18}}{O^{16}}}$$

The same oxygen was used in the preparation of all the samples so that the O^{18}/O^{16}, O^{17}/O^{16} ratios could be considered constant. The values for these ratios were taken as 0·00208 and 0·00039 respectively for tank oxygen as previously determined by Thode and Smith (1944) since our analysis failed to show any significant differences in the ratio of the oxygen isotopes for the tank oxygen used in this investigation.

The isotopic abundances of the sulphur isotopes were measured with a precision of 0·1% or better, although the absolute isotopic abundances are probably only good to ± 1%. The procedure was to analyze the standard sample, the unknown, and then the standard again as quickly as possible. The elapsed time between two standard analyses was approximately 15 minutes. When the two sets of S^{32}/S^{34} ratios for the standard sample agreed with 0·1%, then the comparison with the unknown was considered satisfactory. For each sample the S^{32}/S^{34} ratios were determined for at least six double spectrograms. The internal precision of each analysis was 0·05%.

Preparation of samples

The sulphur dioxide samples used in the mass spectrometer investigation were prepared by standard methods. Sulphide samples of the order of 50–200 milligrams

were burned in a stream of oxygen. One standard source of oxygen is used to prepare all sulphur dioxide samples. The oxygen is passed through activated charcoal at dry ice temperature and concentrated sulphuric acid to remove moisture and hydrocarbon impurities.

The sulphur dioxide is then dried over P_2O_5 and frozen in a trap cooled in liquid air. Carbon dioxide is removed by pumping on the samples at dry ice temperature. Although sulphur dioxide has a vapour pressure of 0·5 mm of Hg, at dry ice temperature, no appreciable fractionation of the sulphur isotopes resulted from this procedure. Mass spectrometer analysis showed carbon dioxide was the only significant impurity in the final sulphur dioxide samples.

Sulphur in the form of metallic sulphide, iron, lead, and zinc, was easily converted to sulphur dioxide and purified by the method described above. However, it was not possible to prepare sulphur dioxide directly from sulphate minerals and be assured of the same concentration of oxygen isotopes as that of the standard oxygen. Therefore, it was necessary to convert the sulphates to combustible sulphides. This was accomplished by two procedures, both of which gave the same relative abundance for the sulphur isotopes and resulted in little or no fractionation of the sulphur isotopes. In the first method the calcium sulphate was converted to calcium sulphide by roasting equal weights of sulphate mineral and carbon powder in a porcelain crucible at 800–1000°C for about 24 hours. The calcium sulphide formed was dissolved in a slightly acidic solution and the sulphur was finally precipitated as lead sulphide.

A second method, which was found to proceed more efficiently than the first method, consisted of mixing excess iron powder with the sulphate in a porcelain crucible, heated over a burner for two hours. The slag formed was treated with hydrochloric acid and the hydrogen sulphide evolved was bubbled through lead acetate solution. In both cases the lead sulphide produced was filtered, washed and dried and burned in a stream of oxygen as described above. Repeated preparation of sulphur dioxide from the same sulphate samples were made to check any possible fractionation of the sulphur isotopes and in no case could any variation in the S^{32}/S^{34} ratio be attributed to the preparation procedures.

Results

The sedimentary samples investigated included shales, sandstones and limestone and were considered to be of marine origin. The sulphur was in the form of visible or finely disseminated pyrite or marcasite. Table 1 gives the source, age and isotopic abundance data for the sedimentary sulphide samples. The deposition ages were taken from a table compiled by Zeuner (1945). It is seen that the S^{32}/S^{34} ratios for these samples vary from 22·08 for the oldest sample to 23·05 for the most recently deposited sample. In Fig. 3 the isotopic ratios are plotted against the geological age at which the sulphides presumably precipitated from solution. Although some scatter of points occurs, there is a striking correlation between geological age and isotopic ratio. From the plot it is seen that very little fractionation of the sulphur isotopes occurred prior to 700 or 800 million years ago. The isotopic ratios obtained for the older samples were essentially the same as those found previously for igneous rock sulphur and meteoritic sulphur. Since

then the sulphur isotopes have become fractionated at an ever increasing rate. The most recent samples investigated are depleted by about 4·4% in S^{34} compared to meteoritic sulphur.

Similar results have been tabulated for samples of sulphate extracted from limestone rock for which some age data is available (Table 2). Although there is a

Table 1. *Sulphur isotope abundances of sulphides in sedimentary rocks of different ages*

Sample	*Location*	*Age* $\times 10^{-6}$ *yrs**	S^{32}/S^{34}
Marcasite Nodule . .	In Chalk, Cambridge, England	80	23·05
Marcasite Nodule . .	In Chalk, Cambridge, England	80	22·95
Deshayesites . . .	France	90	22·90
Cardioceras Concretion	Oxford Clay, Warboys, England	140	22·82
Marcasite Nodule . .	Austin Chalk, Lancaster, Texas	80	22·67
Pyrite	Pyritiferrous Shale, 6 miles west of Grand Falls, Nfd.	250	22·51
Pyrite	Bowland Shale, Bolton Abbey, England	250	22·45
Pyrite	Salty Dolomite, Rocky Mountain Formation, South flank of Mt. Head, Alberta	230	22·38
Pyrite	Huron Shale, Kettle Point, Ontario	300	22·39
Pyrite	Huron Shale, Kettle Point, Ontario	300	22·34
Pyrite	Lockport Dolomite, Lockport, N.Y.	330	22·34
Pyrite	Upper Rundle Formation, Banff, Alberta	250	22·32
Pyrite	Shale, Hudson River Formation, Crawfish Creek, Cincinatti	360	22·30
Pyrite	Keweenawan Sandstone, 1 mile north of Pte. aux Mines, Lake Superior	500–600	22·16
Pyrite	Bruce Conglomerate, Pallideau Island, Bruce Mines, Ontario	750–850	22·11
Pyrite	Waterton Lakes, British Columbia	500–600	22·10
Concretion	McIntyre Mine, Porcupine, Ontario, Archean	1500	22·08

* Ages estimated from best geological data. Geological time scale given by F. E. Zeuner (1945) was used.

Table 2. *Sulphur isotope abundances of sulphates in limestone of different ages*

Sample and Location	*Age* $\times 10^{-6}$ *yrs*	S^{32}/S^{34}
Sandy Limestone, Concrete, Colorado	400–500	22·14
Echo Lake, Ontario, Huronian Limestone	800	22·11
Oolitic Limestone, Bedford, Indiana, Mississippian.	250	22·10
Bruce Limestone, Garden River near Sault Ste. Marie, Ontario .	800	21·99
Vassar College Campus, Trenton, N.Y.	340–390	21·96
Bavaria Solenkofen Limestone, Jurassic	125	21·89
Fossiliferrous Limestone, near Vienna	20	21·81
Mississippian Limestone, Locality Unknown	240	21·98
Sea Water (average)	Present	21·7–21·9

greater scatter of points in this case (see Fig. 3), and the results are less satisfactory from the point of view of sampling, nevertheless the values for the sulphate samples parallel those for the sulphides. The older samples have about the same concentration of S^{34} as have the sulphides, indicating little or no fractionation before 700–800 million years ago. Since then the sulphates have become enriched in

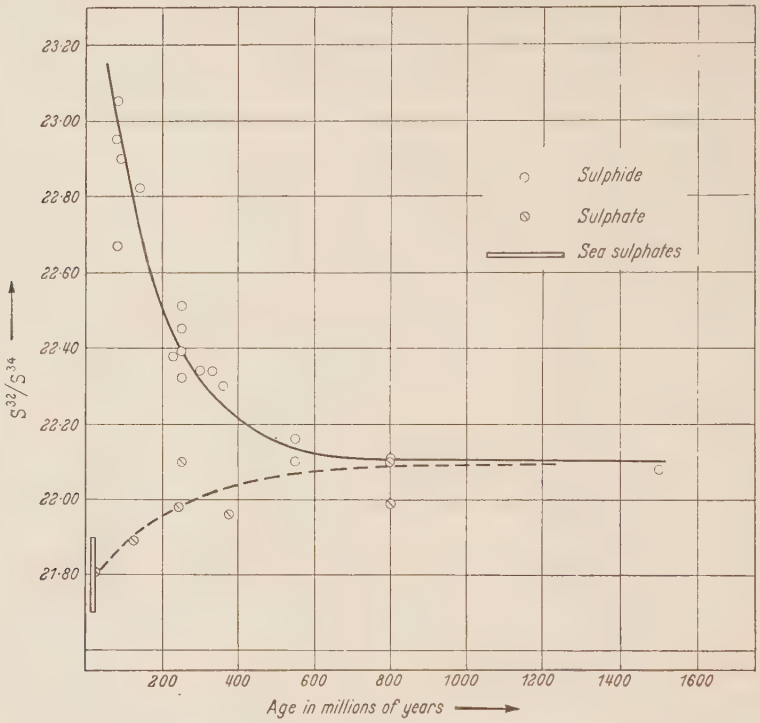

Fig. 3. The distribution of S^{34} in sedimentary sulphides and sulphates of different ages

S^{34} as the sulphides have become depleted in this isotope. It is seen that the overall variations between sulphates and sulphides in marine sediments is about 7·0‰. Insofar as sulphides and sulphates may be changed since deposition in the sedimentary rock, either by dissolution, deposition or by oxidation reduction processes, discrepancies in the age correlation data can be expected.

Discussion

These results strongly support the suggestion made previously (Tudge and Thode, 1950) that fractionation of the sulphur isotopes between sulphides and sulphates has occurred according to the reaction

$$S^{32}O_4^{=} + H_2S \rightleftharpoons S^{34}O_4^{=} + H_2S^{32} \qquad (a)$$

for which the calculated equilibrium constant is 1·074 at 25°C favouring the S^{34} in the sulphate.

It seems fairly certain from experiments carried out previously (Macnamara, 1951; Thode *et al.*, 1951; Macnamara and Thode, 1951) that the biological

sulphur cycle in the sea, illustrated in Fig. 2 can and does provide a mechanism for the fractionation of the sulphur isotopes according to reaction (*a*) above. The importance of biological processes in effecting sulphur isotope fractionation in the sea becomes apparent when one considers their tremendous extent over long periods of time. E. I. Rabinowitch (1945) points out, for example, that all the water in the oceans has been through the photosynthetic process many times since green plants were established on the earth. It is, therefore, conceivable that the sulphides and sulphates in the sea are being turned over at a rapid rate through the biological sulphur cycle.

Sulphides and sulphates are continuously being deposited from the sea and appear in the sedimentary rocks. At the same time the rivers are returning sulphates and sulphides eroded from the rocks to the sea. Volcanoes too are adding sulphur in the different states of oxidation to the system. This inflow and outflow from the exchange processes in the sea would be much like a chemical fractionation process used to separate isotopes, where material is being fed in at one concentration and removed at another. The difference is, of course, that in a natural process essentially only one simple fractionation process is involved.

Recently L. Kulp (1951) has investigated the C^{14} content of organic material in the great depths of the ocean. According to his results these deposits are on the average about 2000 years old. This would suggest that the oceans become completely mixed about every 5000 years. In comparison the building up of sedimentary rocks at the bottom of the seas must be slow and perhaps it can be assumed regarding our age vs. isotope ratio plot that the sea is more or less uniform in isotopic concentration since we are here concerned with variations over hundreds of millions of years.

The isotope ratio vs. geological age plot (Fig. 3), indicates that isotopic fractionation between sulphates and sulphides in the sea began about 800 million years ago and has taken place at an ever-increasing rate since that time. In the most recent samples investigated the maximum spread in the S^{34} content is about 7%. If the biological sulphur cycle is largely responsible for the thermodynamic exchange of S^{34} between sulphides and sulphates in the sea as the evidence suggests, then the results would indicate a marked increase in biological activity over the period 200-350 million years ago. Obviously this increased activity has continued at an accelerated rate.

Sulphur isotope fractionation and the biological time scale

The fact that little or no fractionation occurred prior to 700–800 million years ago suggests that living organisms, which get their free energy to support life from oxidation of H_2S and sulphur did not come into existence much before that time. However, organic matter and living organisms must certainly have been in existence when the sulphur bacteria appeared.

H. C. Urey (1952) has recently outlined the chemical history for the formation of the earth based largely on thermodynamic considerations. According to this outline, the early primitive atmosphere was a reducing one consisting of CH_4, NH_3, H_2 and H_2O. By means of photochemical reactions, many organic compounds were produced, which dissolved in the sea to provide conditions favourable

for the origin of life. This outline of earth history provides the conditions postulated by A. J. Oparin (1938) for life beginning in a reducing atmosphere. The first living organisms according to Oparin and Urey were primitive anaerobes, which got their meagre supply of free energy from the organic compounds in the sea. Then, as these organic compounds became depleted and the atmosphere became more oxidizing through the photosynthesis of water and the loss of H_2 from the planet, living organism began to develop which could utilize the free energy available from the oxidation of sulphur (Van Niel, 1949). These sulphur bacteria are autotrophic and CO_2 and $CO_3^{=}$ provide their only source of carbon. It is believed that the complex process of photosynthesis, in which green plants obtain energy from the sun, came later, perhaps after much of the sulphur had been oxidized to sulphate.

If living organisms evolved as outlined above then it is clear that living organisms could have existed long before the sulphur isotopes began to fractionate about 800 million years ago. What the sulphur isotope studies do give us, however, is a date in the biological time scale when autotrophic organisms utilizing H_2S and $S^{=}$ became significant. This date probably pre-dates the beginning of large-scale photosynthesis.

Further refinements in these studies are being made. Samples of rock are now being investigated which are known to be in chronological order. Further, sulphur isotope studies of oil and coal samples associated with some of the same sedimentary rock beds are being carried out. These studies may provide information concerning the age and origin of oil and thereby be of practical use in oil prospecting.

Acknowledgements—We wish to thank Drs. H. S. Armstrong, D. M. Shaw, and H. S. Scott of our Department of Geology for supplying samples and for many helpful discussions. We also wish to thank Dr. S. Kirkwood for discussions concerning the evolution of living organisms. Finally, we are indebted to the National Research Council of Canada for financial assistance.

References

Graham, R. L., Harkness, A. L. and Thode, H. G.	1947	An A.C. operated mass spectrometer for isotope abundance measurements. J. Sci. Inst. **24**, 119
Kulp, Laurence	1951	Paper presented at the A.A.A.S. meeting, December
Lossing, F. P., Shields, R. B., and Thode, H. G.	1947	A recording unit and electronic shunt selector for a mass spectrometer. Can. J. Research **B25**, 397
Macnamara, J.	1951	Natural variations in the isotopic content of sulphur and their significance. Ph.D. Thesis, McMaster University
Macnamara, J. and Thode, H. G.	1950	Comparison of the isotopic constitution of terrestrial and meteoritic sulphur. Phys. Rev. **78**, 307
Macnamara, J. and Thode, H. G.	1951	The distribution of S^{34} in nature and the origin of native sulphur deposits. Research **4**, 582
Macnamara, J., Fleming, W. H., Szabo, A., and Thode, H. G.	1952	The isotopic constitution of igneous sulphur and the primordial abundance of the terrestrial sulphur isotopes. Can. J. Chem. **30**, 73

Oparin, A. J.	1938	The Origin of Life, MacMillan Company, New York
Rabinowitch, E. I.	1945	Photosynthesis and related processes, 10, Interscience Publishers Inc., New York
Szabo, A., Tudge, A. P., Macnamara, J. and Thode, H. G.	1950	The distribution of S^{34} in nature and the sulphur cycle. Science **3** 464
Thode, H. G. and Smith, S. R.	1944	The natural abundances of the oxygen isotopes. National Research Council of Canada, Montreal Report MC 57
Thode, H. G., Graham, R. L. and Zeigler, J.	1945	A mass spectrometer and the measurement of isotope exchange factors. Can. J. Research **B23**, 40
Thode, H. G., Macnamara, J., and Collins, C. B.	1948	Paper presented at the Royal Society of Canada meeting at Vancouver, B.C.
Thode, H. G., Macnamara, J., and Collins, C. B.	1949	Natural variations in the isotopic content of sulphur and their significance. Can. J. Research **B27**, 361
Thode, H. G., Kleerekoper, H. and McElcheran, D. E.	1951	Isotope fractionation in the Bacterial Reduction of Sulphate. Research **4**, 581
Trafimov, A.	1949	Isotopic composition of sulphur in meteorites and in terrestrial objects. Doklady Akad. Nauk S.S.S.R. **66**, 181
Tudge, A. P. and Thode, H. G.	1950	Thermodynamic properties of isotopic compounds of sulphur. Can. J. Research, **B28**, 567
Urey, H. C.	1951	The origin and development of the earth and other terrestrial planets. Geochim. et Cosmochim. Acta **1**, 209
	1952	**2**, 263
	1952	The Planets, Their Origin and Development, Yale University Press
Van Niel, C. B.	1949	Photosynthesis in Plants, p. 437–495. Iowa State College Press
Zeuner, F. E.	1945	Dating the Past, p. 306, Methuen, London

Geochimica et Cosmochimica Acta, 1953, Vol. 3, pp. 244 to 252. Pergamon Press Ltd., London

Wird das Häufigkeitsverhältnis der Kohlenstoffisotopen bei der Inkohlung verändert?*

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ABSTRACT

Three series of coal samples representing Pliocene, Wealden, and Carboniferous have been investigated. Metamorphism has no traceable influence on the $^{12}C/^{13}C$ ratios. Various factors are briefly discussed in order to explain the observed isotope ratios. Often carbonates in coal do not seem to have been formed from plant carbon dioxide which is contrary to common views on their origin.

Einleitung

In einer früheren Arbeit wurde das Häufigkeitsverhältnis der Kohlenstoffisotopen C–12 und C–13 der heutigen Pflanzenwelt studiert (Wickman, 1952), und es wurde gezeigt, dass verschiedene Biotope charakteristische Unterschiede zeigten. Das leichte Isotop wird an Orten, wo der Kreislauf der Kohlensäure intensiv ist, angereichert, d.h. in tropischen Regenwäldern und stagnierendem Wasser. Weiter schienen die Gymnospermen systematisch eine etwas geringere Anreicherung zu haben als die unter etwa gleichen Bedingungen gewachsenen Angiospermen und Kryptogamen.

Es erhebt sich die Frage, ob diese Befunde durch Metamorphose verändert oder sogar zerstört werden oder ob sie auch für fossile Pflanzen gültig bleiben.

Material und Resultate

Durch die Liebenswürdigkeit von Professor K. Krejci-Graf, Dr. R. Teichmüller und Frau Dr. M. Teichmüller habe ich ein sehr schönes Material erhalten, das von geologisch-stratigraphischen, kohlenpetrographischen und chemischen Gesichtspunkten aus gut untersucht ist. Es sind drei Reihen von Proben,—die erste besteht aus Pliozän-Kohlen von Sumatra, die zweite aus norddeutschen Wealden-Kohlen und die dritte aus oberkarbonischen Kohlen von Nordrhein-Westfalen. Eine genaue Beschreibung der Reihen und die Resultate sind in den Tabellen und in der Diskussion zu finden.

Die Proben wurden zuerst mit Salzsäure gekocht, um etwaige Carbonatmineralien zu zerstören. Von den Wealdenkohlen und den Karbon-Kohlen wurden dabei Bariumcarbonatprobenzur Isotopenbestimmung hergestellt. Ein kleiner Bruchteil von den gereinigten Kohlenproben wurde dann in einem Verbrennungsofen mit Sauerstoff verbrannt. Die Technik war dieselbe, die wir früher in diesem Laboratorium benutzt hatten (Landergren and Parwel, in preparation). Die chemische Präparation wurde von Ing. A. Parwel ausgeführt, wofür ich ihm meinen herzlichen Dank ausspreche.

Die erhaltenen Werte sind nicht als Absolutwerte aufzufassen, sondern sind

* Nr. 6 in einer Reihe von Arbeiten über die Anwendung von Häufigkeitsverhältnissen der Isotopen für geologische Probleme.

Relativwerte, die im Verhältnis zu unserer Standardprobe (WICKMAN *et al.*, 1951) gemessen sind.

Die Isotopenmessungen sind sowohl an den Kohlenproben als auch an den Carbonaten ausgeführt worden. Durch das freundliche Entgegenkommen von Professor E. HAMMARSTEN sind sie im chemischen Laboratorium des Karolinska Instituts in geschickter Weise von Herrn Ing. R. RYHAGE ausgeführt worden. Die Genauigkeit ist dieselbe wie bei der oben besprochenen Pflanzenuntersuchung und die obere Grenze des Messfehlers ist $\pm 0{,}1$ Einheit, doch meistens ist der Fehler kleiner.

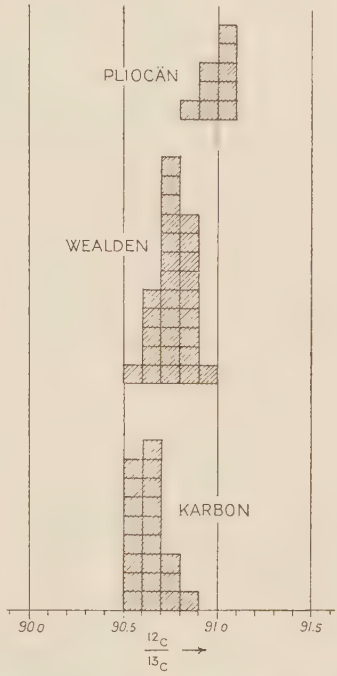

Fig. 1. Die Verteilung der Isotopenquotienten in den drei Inkohlungsreihen.

DISKUSSION DER RESULTATE

Die Resultate sind in Fig. 1 graphisch dargestellt und man sieht, dass die Variationen der drei Kohlenreihen nicht zusammen fallen. Durchschnittlich geben die ältesten Kohlen die kleinsten Isotopenquotienten und die jüngsten die grössten. Bevor diese Verteilung der Werte besprochen wird, ist es zweckmässig, jede Reihe einzeln zu studieren.

(*a*) *Sumatra-Kohlen*

Die von Frau Dr. TEICHMÜLLER mir überlassenen Kohlenproben sind dieselben, die schon von J. W. KREULEN (1935) und A. N. MUKHERJEE (1935) ausführlich untersucht wurden. Sie stammen aus den Tandjoeng-Kohlenfeldern auf Südsumatra. Hier kommen mächtige pliozäne Braunkohlenflöze vor, die durch Wärme andesitischer Magmen metamorphosiert sind. Man findet neben Hartbraunkohle hochwertige Glanzbraunkohle (—"Übergangskohle"), Steinkohle, Anthrazite und Naturkoks.

In den unveredelten Kohlen können Holzreste, Korkgewebe, Harz, Blattreste und Pilzreste (vor allem Sporen und Sklerotien) beobachtet werden. Aber schon in den "Übergangskohlen" sind die organischen Strukturen schwächer erkennbar und in den stark veredelten Kohlen sind diese meist unsichtbar geworden. Die Pflanzenreste zeigen, dass sowohl Angiospermen wie Koniferen vorliegen, wenn auch Koniferenhölzer in den Vitriten bei weitem überwiegen. Trotzdem ist es jedoch nicht möglich, quantitative Angaben zu machen. Denn man muss annehmen, dass in den Tertiärmooren auch Angiospermen wesentlich an der Torfbildung beteiligt waren und nur deswegen in den Kohlen schwer nachweisbar sind, weil Angiospermenholz sich schneller strukturell zersetzt als Koniferenholz.

Tabelle 1 zeigt, dass man in keiner Weise einen Einfluss der Metamorphose auf die $^{12}C/^{13}C$-Werte spüren kann. Die beobachteten Schwankungen sind etwas grösser als die Fehlergrenze, aber man muss annehmen, dass im Laufe der Zeit die Faktoren die den Kohlendioxydzyklus und somit den Anreicherungsgrad im Biotop bestimmen, etwas schwanken.

Es kann also festgestellt werden, dass wenigstens eine Metamorphose, die verhältnismässig schnell verläuft, keinen Einfluss auf das Isotopenverhältnis ausübt.

Tabelle 1

Nr.	*Nach Kreulen* (1935)									$\frac{^{12}C}{^{13}C}$
	Flüchtige Bestandteile %*	*Wasser* %	*Asche* %	C %*	H %*	O + N %*	S %*	*Urteer* %*	*Huminsäure-faktor*	
1	7·2	2·0	2·0	92·6	3·6	2·7	1·1	n. best.	0	90·99
2	11·1	2·3	8·1	89·9	3·8	5·1	1·2	0·1	0	90·91
3	14·8	1·5	1·3	89·8	4·4	4·0	1·8	0·8	0·4	91·02
4	28·4	1·4	1·3	87·5	5·3	6·2	1·0	9·2	6	91·09
5	34·1	1·6	2·1	85·9	5·6	8·5		13·1	20	91·10
6	37·9	2·0	1·6	84·5	5·6	9·9		15·8	12	90·87
7	44·7	5·4	1·6	79·4	5·9	14·7		18·4	97	90·98
8	49·5	9·3	1·9	77·4	5·9	16·7		19·3	167	91·10
9	50·4	8·3	5·5	78·5	6·3	13·8	1·4	20·2	139	91·06

* Bezogen auf wasser–und aschefreie Substanz.

(*b*) *Wealden-Kohlen*

Das Inkohlungsbild des Niedersächsischen Wealdenbeckens ist von M. und R. Teichmüller (1948), untersucht worden. Sie haben ihre Proben sowohl chemisch wie auch petrographisch untersucht und ihre Resultate in Karten zusammengefasst. Es war für meine Untersuchung ein sehr grosser Vorteil, dass sie mir dieses schöne Material zur Verfügung gestellt haben.

Ihre Resultate können kurz auf folgende Weise zusammengefasst werden: weder die Art des Ausgangsmaterials und seine primäre Zersetzung noch der saxonische Faltungsdruck hat auf die Metamorphose der Wealdenkohlen Einfluss

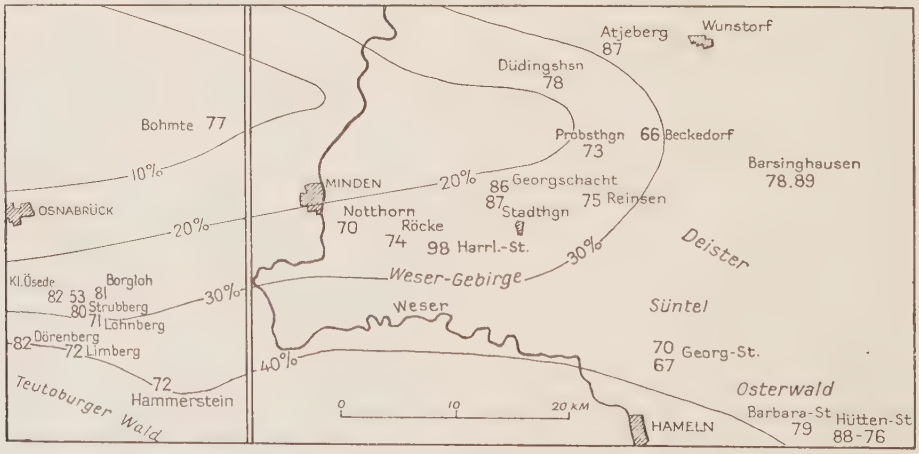

Fig. 2. Die Karte ist nach M. und R. Teichmüller (1948, S.502) gezeichnet und die ausgezogenen Kurven geben den Gehalt an flüchtigen Bestandteilen, bezogen auf Reinkohle im Vitrit, an. Nur die Dezimalen des Isotopenverhältnisses sind in diesem Bilde eingetragen. Alle Proben haben 90, . . . gemeinsam.

gehabt. Allein die verschiedene Erhitzung der Kohlen durch die verschiedene Versenkungstiefe und die regional offenbar einst recht verschiedene geothermische

Tabelle 2

Nr.	*Wealdenkohle*	*flücht. Best.* $\%waf$[1]	C% (C + H + O = 100)[1]	C^{12}/C^{13}	$\%CaCO_3$	C^{12}/C^{13}
1	Bohmte (NO Osnabrück)	9·4	93·2	90·77	1·5	88·56
2	Bohrung Probsthagen 1,646 m	14·1	92·8	90·73	1·2	88·97
3	Flöz 4, Notthorn bei Minden	19·6	92·1	90·70	0	—
4	Flöz 3, Georgschacht bei Stadthagen	21·0	91·6	90·87	0·6	87·87
5	Flöz 3, Reinsen	21·7	92·2	90·75	0	—
6	Flöz 3, Georgschacht bei Stadthagen	21·9	91·9	90·86	1	87·86
7	Flöz 3, Beckedorf	24·1	90·2	90·66	0·5	88·34
8	Flöz 4, Rökke bei Minden	24·3	90·3	90·74	0	—
9	Flöz Dickebank, Kloster Oesede	25·8	90·5	90·82	1	88·70
10	Harrl bei Bückeburg	25·8	88·3	90·98	0	—
11	Flöz 3, Strubberg (Teutoburger Wald)	27·3	86·4	90·53	0	—
12	Flöz 3, Oberbank, Elbendorf (Teutoburger Wald)	27·8	90·0	90·81	0	—
13	Flöz 3, Düdinghausen	29·2	98·0	90·78	0	—
14	Flöz 4, Strubberg (Teutoburger Wald)[2]	30·6	78·1	90·80	0	—
15	Flöz 3, Borgloh (Teutoburger Wald)	31·2	88·3	90·81	0	—
16	Flöz 3, Atjeberg	32·7	88·4	90·87	0	—
17	Lohnberg (Teutoburger Wald)	33·9	86·9	90·71	0	—
18	Flöz 3, Barsinghausen	34·0	86·1	90·78	0	—
19	Flöz 3, Barsinghausen	34·0	87·2	90·89	0	—
20	Osterwalder Liegendflöz, Hüttenstollen	35·2	84·9	90·76	0	—
21	Kupferschieferflöz, Georgstollen (Süntel)	36·2	85·7	90·70	0	—
22	Flöz 3, Georgstollen (Süntel)	36·3	85·1	90·67	0·3	90·32
23	Hammerstein (TeutoburgerWald)	36·4	86·2	90·72	0	—
24	Osterwalder Hangendflöz Hüttenstollen	39·0	84·6	90·88	0	—
25	Osterwalder Hangendflöz, Barbarastollen	39·4	84·2	90·79	0	—
26	Bocketal bei Ibbenbüren[2]	42·9	75·3	90·65	0	—
27	Dörenberg (Teutoburger Wald)	43·7	82·8	90·82	0	—
28	Limberg (Teutoburger Wald)	44·2	82·7	90·72	0	—

(1) Nach M. u. R. Teichmüller waf = bezogen auf wasser–und aschefreie Substanz.
(2) Stark oxydierte Proben.

Tiefenstufe scheint für die Inkohlungsunterschiede verantwortlich gewesen zu sein. Wahrscheinlich hängt diese starke Metamorphose im Zentrum des Niedersächsischen Beckens damit zusammen, dass es in der Tiefe junge magmatische

Intrusionen gibt, die auch andere Forscher auf Grund ganz verschiedener Indizien vermuteten. In Abb. 2 (S. 502) der oben erwähnten Arbeit von M. u. R. Teichmüller ist die Metamorphose des Gebietes klar gelegt und der Leser wird auf die detaillierte Beschreibung in dieser Arbeit verwiesen.

Die Flora der Wealden-Moore wird nach Angaben von Frau Dr. Teichmüller überwiegend aus Gymnospermen bestanden haben. Aber auch Pteridophyten, vor allem Farne, waren an der Torfbildung beteiligt.

Die Isotopenquotienten zusammen mit den Inkohlungsdaten von Teichmüller sind in Tabelle 2 zusammengestellt und mit Ausnahme von der Probe Bocketal, die zu westlich liegt, sind alle Kohlenwerte in Figur 2 eingetragen. Die ausgezogenen Kurven geben den Gehalt an flüchtigen Bestandteilen, bezogen auf Reinkohle im Vitrit (nach M. u. R. Teichmüller) an. Der Gehalt an flüchtigen Bestandteilen ist ja ebenso wie der C-Gehalt ein Mass der Metamorphose der Kohle. Infolgedessen geht aus der Tabelle und dem Bild ganz deutlich hervor, dass man auch hier keinen Einfluss der Metamorphose auf die relative Häufigkeit der Kohlenstoffisotopen festellen kann. Dies steht völlig im Einklang mit dem, was wir schon bei dem Material aus Sumatra gefunden haben.

Aus Tabelle 2 ist ersichtlich, dass einige Proben etwas Carbonat enthalten. Da man oft zusammen mit Kohlen Siderit und Dolomit findet, sind die Carbonatwerte als Calciumcarbonat umgerechnet, denn dann wird die Korrektion in beiden Fällen so klein, dass sie für unsere Zwecke vernachlässigt werden kann. Es ist auffällig, wie die Werte schwanken. In Probe 9 hat man wohl mit einem Carbonat zu tun, das hauptsächlich aus organischem Kohlenstoff entstanden ist. Die beiden Proben aus dem Georgschacht bei Stadt Hagen (Nr. 4 und 6) haben die niedrigsten Werte ergeben, die wir überhaupt bisher beobachtet haben.

(c) *Karbonkohlen aus Rheinland-Westfalen*

Von Dr. M. und R. Teichmüller habe ich auch eine Reihe von genau untersuchten Kohlenproben aus dem Karbon von Rheinland-Westfalen bekommen. In diesem Gebiet gilt in der Hauptsache dié sogenannte Hiltsche Regel (Böttcher *et al.*, 1949) d.h. der Inkohlungsgrad nimmt mit der ursprünglichen Versenkungstiefe, also mit zunehmender thermischer Beanspruchung der Flöze zu. Ein Einfluss des Faltungsdruckes auf die Inkohlung ist hier wie auch im Niedersächsischen Wealdenbecken nicht feststellbar.

Kohlenbildende Pflanzen der Karbonmoore waren nach Angabe von Frau Dr. Teichmüller vor allem Pteridophyten, daneben Gymnospermen und Übergangstypen (Pteridospermen).

Die Resultate sind in Tabelle 3 zusammengestellt. Man kann wieder keine Tendenz in dem Schwanken der Werte finden. Man könnte vielleicht glauben, dass Proben, die arm an flüchtigen Bestandteilen und reich an C sind, kleinere Werte geben sollten. Wenn es eine solche Verschiebung gibt, ist sie jedoch so klein, dass sie innerhalb der Fehlergrenze liegt.

Auch hier kommen Carbonate vor und ihre Isotopenquotienten sind ebenfalls uneinheitlich, aber sie liegen doch dichter zusammen als bei den Wealden-Kohlen. Es ist möglich, dass die verschiedenen Zechen durch gewisse Schwankungsbereiche charakterisiert sind, je nachdem ob epigenetischer Kluftspat oder syngenetische

Carbonate vorherrschen. Aber dies ist nicht eindeutig bewiesen, weil die Anzahl der Werte zu gering ist.

Tabelle 3. *Karbonkohlen aus Nordwestdeutschland*

Nr.	*Fundort*	*Kohle*			*Calciumcarbonat*	
		% *flücht.* B.[1] *waf*[2]	%C[1] (C + H + O = 100)	$^{12}C/^{13}C$	*Gewichts* %	$^{12}C/^{13}C$
1	33 cm Flöz, Zeche Laurweg, Aachen	6·7	94·9	90·56	0	—
2	2. Riffel unter Flöz Furth, Zeche Maria, Aachen	12·6	92·8	90·54	0·5	88·89
3	51 cm Flöz, Zeche Maria, Aachen	14·0	92·1	90·59	0	—
4	Flöz E P1MB, Zeche Maria, Aachen	15·0	93·3	90·65	0·5	89·07
5	Flöz E RMB, Zeche Maria, Aachen	15·7	93·0	90·64	1	89·12
6	Flöz Flottwell, Ibbenbüren	16·2	92·3	90·78	20	89·51
7	Flöz Finefrau, Zeche Neu-Iserlohn	17·0	93·1	90·52	1	88·76
8	Flöz Sonnenschein, Zeche Neu-Iserlohn	19·1	91·2	90·67	3	88·76
9	Flöz Finefrau, Zeche Neu-Iserlohn	20·0	91·0	90·67	1	88·23
10	Flöz Sonnenschein, Zeche Neu-Iserlohn	20·9	90·9	90·66	0·3	88·51
11	Flöz Helene, Zeche Neu-Iserlohn	22·6	90·0	90·79	3	88·54
12	Flöz Luise, Zeche Neu-Iserlohn	22·6	90·9	90·58	1	88·36
13	Flöz Sonnenschein, Minister Stein	24·4	90·3	90·51	0	—
14	Flöz Karoline, Zeche Minister Stein	26·5	86·8	90·65	0	—
15	Flöz Wilhelm, Zeche Minister Stein	27·9	86·9	90·73	0	
16	Flöz C, Zeche Fritz-Heinrich	33·3	86·3	90·62	0·5	89·53
17	Flöz Kobold, Zeche Brassert	36·3	79·8(?)	90·60	3	89·46
18	Flöz Freya, Zeche Fürst Leopold	36·3	82·9	90·59	0	—
19	Flöz Baldur, Zeche Fürst Leopold	37·0	84·2	90·89	0·5	89·49
20	Flöz Freya, Zeche Fürst Leopold	38·0	82·5	90·65	0	—
21	Flöz Freya, Zeche Fürst Leopold	42·4	84·0	90·61	0	—

[1] Nach M. und R. Teichmüller.
[2] Bezogen auf wasser–und aschefreie Substanz.

Allgemeine Gesichtspunkte

Das Mittel für die Isotopenverteilung in den drei Kohlenvorkommen ist für Karbonkohle 90·64, Wealdenkohle 90·77 und Pliozänkohle 91·01. Man hat also tatsächlich verschiedene Werte bekommen, die eine steigende Tendenz mit

abnehmendem Alter zeigen. Der Grad der Metamorphose (Inkohlung) spielt dabei keine Rolle. Dieselbe Tatsache ist aus Abb. 1 zu entnehmen.

Wie soll man dies verstehen? Hat sich die Zusammensetzung der Atmosphäre geändert? Oder soll man annehmen, dass diese Werte Unterschiede zwischen den Biotopen ausdrücken?

Es ist natürlich unmöglich, aus unserem kleinen Material sichere Beweise für die eine oder andere Ansicht zu finden, aber einige Tatsachen sind von Interesse.

Wie schon erwähnt, bestehen die Pliozänkohlen aus Gymnospermen und Angiospermen, wenn es auch auf Grund des schlechten Erhaltungszustandes vieler Pflanzenreste unmöglich ist, die Prozentzahlen zu bestimmen. Die Wealdenkohle dürfte überwiegend aus Gymnospermen bestehen und die Karbonkohle aus Pteridophyten und Gymnospermen bzw. Übergängen in Form der Pteridospermen.

In einer früheren Untersuchung (Wickman, 1952) wurde die heutige Pflanzenwelt untersucht. Dabei wurde gefunden, dass die untersuchten Gymnospermen zwischen 90·48 90·80 schwanken mit dem Schwerpunkt ungefähr zwischen 90·60–90·65. Die gymnospermenreichen Wealdenkohlen geben auffallenderweise etwas höhere Werte. Gegenwärtig gibt es ja nicht so viele Pteridophyten, aber die vier untersuchten Proben von *Lycopodinae* geben Werte, die zwischen 90·72–91·03 schwanken. Die pteridophytenreichen Karbonkohlen haben im Gegensatz zu den gymnospermenreichen Wealdenkohlen in den meisten Fällen kleinere Werte.

Man kann aber auch ohne Rücksicht auf die systematische Stellung der Pflanzen einmal die ökologischen Bedingungen, unter denen die Moorpflanzen gewachsen sind, einer Betrachtung unterziehen.

Die Pliozänkohlen sind wohl unter denselben Bedingungen entstanden, die auch heute noch in den Waldmooren von Sumatra herrschen, d.h. in einem tropischen Regenwald. Es ist ja auch so, dass alle untersuchten Pliozänkohlenproben Werte geben, die mit denen heutiger Regenwaldpflanzen (90·8–91·4) direkt vergleichbar sind.

Für die Wealdenkohlen und auch die Karbonkohlen ist es nicht so leicht, einen entsprechenden Vergleich zu finden, denn wahrscheinlich haben klimatische Verhältnisse und die Vegetationsbilder während ihrer Entstehung geschwankt, so dass man sich kein einheitliches Bild machen kann. Wenn z.B. die Verhältnisse verglichen werden mit denen, die heute in den Everglades von Florida herrschen, wo Bruchwald, Ried und offene Wasserflächen horizontal einander ablösen, so müsste man mittlere Werte erwarten. In der früher erwähnten Arbeit (Wickman, 1952) ist auch eine Pflanze aus den Everglades gemessen worden, nämlich *Eugenia buxifolia* (Nr. 62), die den Wert 90·70 gibt. Auch andere Pflanzen, die in küstennahen Gegenden gewachsen sind, geben Werte, die mit denen der Fossilen übereinstimmen. Weitere lokale Faktoren können ebenfalls einwirken. Es ist also nicht berechtigt, aus der vorliegenden Untersuchung den Schluss zu ziehen, dass die Isotopenzusammensetzung der Luftkohlensäure sich verändert hat. Dies ist durchaus möglich, aber die Lösung dieses Problems muss der Zukunft überlassen werden.

Interessant ist es, dass die gymnospermenreichen Wealdenkohlen höhere Werte geben als die lebenden Gymnospermen. Darum ist es wichtig, dass man umfassende Untersuchungen über die heutigen Gymnospermen durchführt.

Die Untersuchung der in den Kohlen vorkommenden Carbonate ergab interessante Einzelheiten. Hier sind sie als Calciumcarbonat berechnet, aber es ist—wie schon erwähnt natürlich auch möglich, dass sie als Eisencarbonat oder Dolomit vorliegen. Jedoch hat dies keinen Einfluss auf die Isotopenwerte, man bekommt nur eine kleine Korrektion des Gehaltes in Gewichtsprozenten. Die Werte sind in Fig. 3 ohne Rücksicht auf das geologische Alter dargestellt.

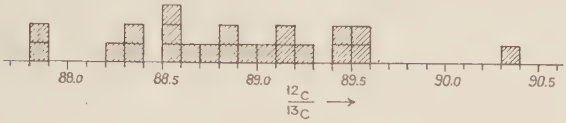

Fig. 3. Die Verteilung der Isotopenquotienten in den Carbonaten der Inkohlungsproben.

Auffallend sind die grossen Schwankungen der Werte und die Tatsache, dass nur einmal in 21 Fällen ein Wert über 90 beobachtet wurde. Die meisten Proben geben Werte etwas unter 89, d.h. Werte, die an sich typisch für marine Kalksteine sind. Die Zwischenwerte—wohl über 89 –können entweder durch Mischung von Kalksteinkohlensäure und Pflanzenkohlensäure entstanden sein, oder, was nach meiner Ansicht noch wahrscheinlicher ist, durch Grundwasserkohlensäure.

Nach Vorstellung gewisser Autoren (Moore, 1940; Potonié, 1924) sind Carbonate, die zusammen mit Kohlen gefunden werden, zumeist aus dem Kohlendioxyd, das bei der Inkohlung (vor allem im biochemischen Stadium) gebildet wird, entstanden. Dies ist durchaus wahrscheinlich. Denn insbesondere bei der frühen Inkohlung entstehen grosse Mengen von Kohlensäure und in vielen Braunkohlengruben besteht das Grubengas in der Hauptsache aus Kohlendioxyd. Es mag aber schon hier erwähnt werden, dass auch nach anderen Beobachtungen, die ich gemacht habe, Sideritkonkretionen in Steinkohlen nicht von "Pflanzenkohlensäure" gebildet wurden. Wahrscheinlich ist das Carbonat hier älter als die eigentliche geochemische Inkohlung und folglich syngenelisch gebildet.

Zusammenfassung

Drei Reihen von verschieden alten Kohlenproben sind untersucht worden. Die erste (pliozäne) Reihe ist von einem andesitischem Magma metamorphosiert worden, die zweite (aus dem Wealden) und die dritte (aus dem Karbon) sind ebenfalls thermisch metamorphosiert, wenngleich nicht durch direkte Kontaktmetamorphose. In keinem Fall war es möglich, einem Einfluss der Metamorphose auf die Isotopenverteilung festzustellen.

Die drei Reihen geben deutlich verschiedene Durchschnittswerte der Isotopenverhältnisse. Jedoch erlaubt dies keinen Schluss auf eine zeitliche Variation des Isotopenverhältnisses der Luftkohlensäure.

Die Carbonate, die in den Kohlen in geringen Mengen vorkommen, sind in den meisten Fällen wohl aus Grundwasserkohlensäure, nur ausnahmsweise aus Pflanzenkohlensäure gebildet.

Schrifttum

Böttcher, H., Teichmüller, M. u. R. 1949 Zur Hiltschen Regel in der Bochumer Mulde des Ruhrkarbons. Glückauf **85**, 81

Kreulen, J. W. 1935 Grundzüge der Chemie und Systematik der Kohlen. Amsterdam

Landergren, S. and Parwel, A.		On the relative abundance of the carbon isotopes in marine sediments. Geochim. et Cosmochim. Acta. In preparation.
Moore, E. S.	1940	Coal. 2 Ed., New York
Mukherjee, A. N.	1935	Ein Beitrag der pliocänen Braunkohle des Tandjoeng Kohlenfeldes Palembang, Südsumatra. Diss. Sächs. Bergakad. Freiberg
Potonté, R.	1924	Einführung in die allgemeine Kohlenpetrographie. Berlin
Teichmüller, M. u. Teichmüller, R.	1948	Das Inkohlungsbild des Niedersächsischen Wealden-Beckens. Z.Dtsch. Geol. Ges. **100**, 498
Wickman, F. E., Blix, R. and von Ubisch, H.	1951	On the variations in the relative abundance of the carbon isotopes in carbonate minerals. J. Geol. **59**, 142
Wickman, F. E.	1952	Variations in the relative abundance of the carbon isotopes in plants. Geochim. Cosmochim. Acta **2**, 243

Geochimica et Cosmochimica Acta, 1953, Vol. 3, pp. 253 to 256. Pergamon Press Ltd., London

Comparative measurements of standards for carbon isotopes

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ABSTRACT

Measurements on two American, one Swedish and one Danish standard for carbon isotopes are reported. These measurements are intended to provide a direct comparison between American and Scandinavian measurements on carbon isotopes. CO_2 samples are used in the mass-spectrometry and it is shown that differences in O^{17}-abundance may cause measurable errors.

Lately much work has been done in determining the abundance of the heavy carbon isotope C^{13} in nature. The great accuracy with which such measurements can be made has made it desirable to consider carefully the basis on which they depend.

The abundance of carbon isotopes in a given sample is often stated by the numerical ratio of C^{12} to C^{13}-atoms, characterized in this paper by C^{12}/C^{13}. Mass-spectrographic determination of this ratio is very difficult, but differences in C^{12}/C^{13} can be found with great accuracy. A standard is chosen, and results are normally reported either simply as the difference from the standard or as the C^{12}/C^{13}-value obtained from attaching some value to the standard and adding the difference measured. Neither of these procedures, however, permits of comparison with other results, unless the differences are known between the particular standards that were used.

Professors A. O. Nier and H. C. Urey have each kindly supplied samples of their standards ($CaCO_3$; in this paper called *N* and *U* respectively). A comparison has therefore been made of each of these with a Swedish standard ($BaCO_3$; called *S*) from Naturhistoriska Riksmuseum in Stockholm and a Danish one (bomb-CO_2; called *D*).

The measurements were made with a Consolidated-Nier Isotope-Ratio Mass Spectrometer, model 21–201. In this instrument it is necessary to admit each sample of carbon in the form of CO_2. The combustion of the solid standards can be achieved in different ways. Some investigators use H_3PO_4, others HCl and, in Sweden $BaCO_3$ is heated together with NaH_2PO_4. These procedures are indicated in this paper by H_3PO_4, HCl and NaH_2PO_4 respectively.

After ionization of the CO_2-molecules in the mass spectrometer an electromagnetic deflection of their paths takes place, so that all singly charged ions with the same mass are focused and measured together. The instrument primarily gives a value for 45/44, i.e. the ratio of quantities between ions with mass 45 ($C^{13}O_2{}^{16}$ and $C^{12}O^{16}O^{17}$) and ions with mass 44 ($C^{12}O_2{}^{16}$).

The values of 45/44 for the Swedish and the American standards were found to be higher than the Danish, and the differences from the Danish 45/44, have been recorded in Table 1. In the main part of this table the figure after "$\pm$" indicates the reproducibility of the last figure on the particular day. In the last line, however, it means the standard deviation of the mean.

Table 1. *Differences above the Danish value* ($\times 100$) *of* 45/44

Preparation	*N* H_3PO_4	*U* H_3PO_4	*S*
1951, Aug. 21			0·0144 ± 5 (NaH_2PO_4)
Dec. 10			0·0142 ± 2 (NaH_2PO_4)
,, 11			0·0132 ± 3 (NaH_2PO_4)
,, 12			0·0133 ± 3 (NaH_2PO_4)
,, 13			0·0138 ± 3 (H_3PO_4)
,, 14			0·0141 ± 3 (NaH_2PO_4)
,, 15	$0·0262_5$ ± 2		
,, 15	$0·0261_5$ ± 2		
1952, Mar. 9	0·0262 ± 2		
Jun. 16			0·0136 ± 2 (HCl)
Aug. 10	$0·0264_5$ ± 2	0·0281 ± 6	
,, 11		0·0289 ± 4	
Mean	0·02625 ± 7	0·0285 ± 4	0·0138 ± 2

It is seen that the combustion method does not affect the result.

If NIER'S measurement of the standard "Jurassic Limestone, Solenhofen, Bavaria" (NIER, 1950) is used as basis with the C^{13}/C^{12}-value of 1·124% ±0·003 (here ±0·003 refers to 1·124 as an absolute value), and if it is presupposed that the O^{17}-abundance is the same in all the standards (so that no corrections for $C^{12}O^{16}O^{17}$ are necessary, since they disappear in forming the differences) the values given in Table 2 are now found.

Table 2

	N	*U*	*S*	*D*
C^{13}/C^{12}	1·124%	$1·126_3$%	$1·111_6$%	$1·097_8$%
C^{12}/C^{13}	$88·9_7$	$88·7_9$	$89·9_6$	$91·0_8$

However, the presupposition does not hold, as can be seen by measuring the O^{18}-abundance. This is feasible by measuring 46/(44 + 45), i.e. the ratio between ions of mass 46 ($C^{12}O^{16}O^{18}$ mainly) and ions of the masses 45 ($C^{13}O_2{}^{16}$ and $C^{12}O^{16}O^{17}$) and 44 ($C^{12}O_2{}^{16}$). Against 46/44 in Table 3 the results are corrected for differences in C^{13}- as well as in O^{17}-abundance. It is clear that the standards have not the same O^{18}-abundance.

In order to ascertain the consequence of any differences in O^{17}-abundance, CO_2 from each standard was shaken with excess of distilled water. An exchange of oxygen atoms then takes place between CO_2 and H_2O, for example

$$CO_2{}^{16} + H_2O^{17} \rightleftharpoons CO^{16}O^{17} + H_2O^{16},$$

and if an excess of water exists, the CO_2 will after some time have an O^{17}-abundance

Table 3

	N	*U*	*S*	*D*	*N*, *U*, *S* and *D* *after exchange*
	%	%	%	%	%
46/(44 + 45)	0·4242	0·4263	0·4170	0·4174	0·4221
46/44	0·4293	0·4316	0·4219	0·4223	0·4271
Difference from D	0·0070	0·0093	−0·0004		

which corresponds to that of the water. Cohn and Urey (1938) mention 3 hours as the shaking time required. In my first experiment 64 hours and in the others not below 8 hours were used. That oxygen exchange was complete was checked by measuring 46/44 which gave the same value for the four samples.

Table 4

	N	*U*	*S*
	%	%	%
1952, Aug. 11	0·0241 ± 3	0·0252 ± 3	
Aug. 13	0·0229 ± 3	0·0252 ± 3	0·0137 ± 3
Aug. 15	0·0236 ± 3	0·0250 ± 3	
Mean	0·0235 ± 4	0·0251 ± 1	0·0137 ± 3

The differences in 45/44 (now identical with differences in C^{13}/C^{12}) between *N*, *U* and *S* with *D* after dessication with liquid air are recorded in Table 4. As anticipated from the very small difference in 46/44 between *S* and *D*, the difference in 45/44 between these two was not changed, whereas *N* and *U* were changed considerably.

From the values in Table 4, and taking as basis 1·124% for C^{13}/C^{12} in *N*, Table 5 was obtained.

Table 5

	N	*U*	*S*	*D*
C^{13}/C^{12}	1·124%	$1{\cdot}125_6$%	$1{\cdot}114_1$%	$1{\cdot}100_4$%
C^{12}/C^{13}	$88{\cdot}9_7$	$88{\cdot}8_4$	$89{\cdot}7_6$	$90{\cdot}8_8$

If in conformity with what is done in defining some physical magnitudes we put the C^{13}/C^{12}-value of Nier's standard at 1·1240%, corresponding to 88·97 for C^{12}/C^{13}, the other standards will acquire the values in Table 6. The error of these relative values of C^{12}/C^{13} scarcely exceeds 0·06.

Table 6

	N	*U*	*S*	*D*
C^{13}/C^{12}	1·1240%	1·1256%	1·1141%	1·1004%
C^{12}/C^{13}	88·97	88·84	89·76	90·88

Table 7

	N	*U*	*S*	*D*
	%	%	%	%
Difference from *D* (before exchange)	0·0262 ± 1	0·0285 ± 4	0·0138 ± 2	0·0000
Difference from unexchanged *D* (after exchange)	0·0257 ± 4	0·0268 ± 3	0·0165 ± 3	0·0028 ± 3
Change in 45/44	−0·0005 ± 4	−0·0017 ± 5	0·0027 ± 4	0·0028 ± 3
Change in 46/44	−0·0022 ± 4	−0·0035 ± 4	0·0052 ± 4	0·0048 ± 4

If we look at the changes in 45/44 and 46/44 caused by the oxygen exchange we get the values in Table 7, the last line of which is taken from Table 3. It is evident that differences in O^{17}-abundance between sample and standard may cause measurable deviations if they are not taken into consideration. To secure the same O^{17}-abundance in standard and sample, the most rational way is to allow both of them to exchange with water. Failure to do so may involve an error of at least 0·36 in C^{12}/C^{13} or 0·0045% in C^{13}/C^{12}. This is evident in Table 7 from the O^{17}-difference before the exchange between *U* and *D*, giving

$$(0{\cdot}0028 \pm 3) + (0{\cdot}0017 \pm 5) = 0{\cdot}0045\% \pm 6$$

when $C^{13}/C^{12} = 1{\cdot}1\%$ approximately. This means that the absolute error of C^{13}/C^{12} may amount to 0·0045% or even more, merely as a consequence of difference in O^{17}-abundance.

REFERENCES

COHN, M. and UREY, H. C. 1938 J. Amer. Chem. **60**, 679

NIER, A. O. 1950 Phys. Rev. **77**, 789

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